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L. INFELD

Comité de Rédaction de la Série
K. BORSUK, S. LESZCZYCKI, J. SAMSONOWICZ, M. ŚMIAŁOWSKI

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MATHEMATICS

A Fixed Point Theorem for Completely Continuous Operators in Banach Spaces

by

M. ALTMAN

Presented by K. BORSUK on June 8, 1955

The known theorem on antipodes of K. Borsuk [1] (cf. [2]) was extended by M. A. Krasnoselsky [3] for the case of completely continuous operators in Banach spaces.

Recently M. A. Krasnoselsky [4] has proved a generalisation of Borsuk's theorem on antipodes for the case of an n-dimensional Euclidean sphere, which consists in replacing the antipodal mapping by a continuous involution. This result was also obtained (independently) by J. W. Jaworowski [5] as a corollary of a more general argument.

In the present note we prove a theorem which is in some sense an extension of the above mentioned theorems for the case of completely continuous operators on the sphere in a Banach space.

Denote by Q the sphere, defined in a Banach space E by the inequality $\|x\| \leqslant 1$, and by S the boundary of Q.

Let F be a completely continuous operator *) (in general non-linear) defined on S with domain in E. Consider the continuous operator

$$\Phi = F - I,$$

defined on S, where I is the identical transformation of E. Suppose that

$$\Phi(x) \neq \Theta \quad \text{for every} \quad x \in S, \tag{1}$$

where Θ is the zero-element in E. It is easy to see by (1) that there exists a positive number a such that

$$\|\Phi(x)\| > a \quad \text{for every} \quad x \in S. \tag{2}$$

*) An operator F is said to be completely continuous if it is continuous and its image is a compact set.

Further, let U be a continuous dimension non-rising involution of S onto itself without a fixed point, i. e. a continuous dimension non-rising *) mapping U such that $U(U(x))=x$ for every $x \in S$.

Then the following theorem is true.

THEOREM 1. *Let us assume that on the boundary S of the sphere Q is defined a continuous mapping $\Phi(x)=F(x)-x$, where F is a completely continuous operator, satisfying condition* (1) *and let U be a continuous dimension non-rising involution satisfying the following condition*

$$\inf_{x \in S} \left\| \frac{\Phi(x)}{\|\Phi(x)\|} - \frac{\Phi(Ux)}{\|\Phi(Ux)\|} \right\| = \beta > 0. \tag{3}$$

Then the degree **) *of Φ is odd.*

Proof. Following Leray and Schauder [6] we choose in E a finite-dimensional linear subspace E_n containing an ε-net of the compact set $F(S)$ as follows. Let E_p be the finite-dimensional linear space spanned by an ε-net of the set $F(S)$ and $x_1, x_2, \ldots, x_p$ a normed basis in E_p. Denote by E_n the linear space spanned by the elements $x_1, x_2, \ldots, x_p$ and $U(x_1), U(x_2), \ldots, U(x_p)$. Since the mapping U is dimension non-rising, the image $U(S^{(n-1)})$ of the sphere $S^{(n-1)}=S \cap E_n$ is contained in an $(n-1)$-dimensional sphere. But this sphere contains all elements x_i, $U(x_i)$ $(i=1,2,\ldots,p)$ and therefore it coincides with $S^{(n-1)}$. Thus the mapping U is a homeomorphism of $S^{(n-1)}$ into itself, whence we conclude that U is an involution of $S^{(n-1)}$ onto itself.

Let P_ε be a continuous projection operator, defined on $F(S)$ with domain in E_n, such that

$$\|P_\varepsilon F(x) - F(x)\| < \varepsilon \quad \text{for} \quad x \in S, \tag{4}$$

where

$$\varepsilon < \frac{a}{2}.$$

We define now on $S^{(n-1)}=S \cap E_n$ a continuous operator by the formula

$$\Phi_\varepsilon(x) = P_\varepsilon F(x) - x \quad \text{for} \quad x \in S^{(n-1)}. \tag{5}$$

We shall show that the mapping $\dfrac{\Phi(x)}{\|\Phi_\varepsilon(x)\|}$ satisfies the conditions of the theorem of Krasnoselsky – Jaworowski [4], [5].

In fact, the values of $\Phi_\varepsilon(x)$ on $S^{(n-1)}$ are different from the zero-element, since by (2) and (4) we have

$$\|\Phi_\varepsilon(x)\| \geqslant \|F(x)-x\| - \|P_\varepsilon F(x) - F(x)\| > \frac{a}{2} \quad \text{for} \quad x \in S^{(n-1)}. \tag{6}$$

*) i. e. the image of an n-dimensional sphere lies in an n-dimensional one, for almost all positive integers n.

**) i. e. the degree $d[\Phi, Q, 0]$ in the sense of Leray – Schauder [6].

Further, we have

$$\left\| \frac{\Phi_\varepsilon(x)}{\|\Phi_\varepsilon(x)\|} - \frac{\Phi_\varepsilon(Ux)}{\|\Phi_\varepsilon(Ux)\|} \right\| \geqslant \tag{7}$$

$$\geqslant \left\| \frac{\Phi_\varepsilon(x)}{\|\Phi_\varepsilon(x)\|} - \frac{\Phi(x)}{\|\Phi(x)\|} \right\| + \left\| \frac{\Phi(x)}{\|\Phi(x)\|} - \frac{\Phi(Ux)}{\|\Phi(Ux)\|} \right\| - \left\| \frac{\Phi(Ux)}{\|\Phi(Ux)\|} - \frac{\Phi_\varepsilon(Ux)}{\|\Phi_\varepsilon(Ux)\|} \right\|.$$

The set $F(S)$ is bounded, since it is compact. Hence there exists a positive number K such that

$$\|F(x)\| \leqslant K \quad \text{for} \quad x \in S. \tag{8}$$

We have

$$\frac{\Phi_\varepsilon(x)}{\|\Phi_\varepsilon(x)\|} - \frac{\Phi(x)}{\|\Phi(x)\|} = \frac{P_\varepsilon F(x) - x}{\|P_\varepsilon F(x) - x\|} - \frac{F(x) - x}{\|F(x) - x\|} =$$

$$= \frac{\|F(x)-x\|(P_\varepsilon F(x) - F(x)) + (\|F(x)-x\| - \|P_\varepsilon F(x) - x\|) F(x)}{\|P_\varepsilon F(x) - x\| \cdot \|F(x) - x\|} - \tag{9}$$

$$- \frac{(\|F(x)-x\| - \|P_\varepsilon F(x) - x\|) x}{\|P_\varepsilon F(x) - x\| \cdot \|F(x) - x\|}.$$

By virtue of (2), (4), (6), (8) and (9) we obtain the inequality

$$\left\| \frac{\Phi_\varepsilon(x)}{\|\Phi_\varepsilon(x)\|} - \frac{\Phi(Ux)}{\|\Phi(Ux)\|} \right\| \leqslant \frac{(K+1)\varepsilon + K\varepsilon + \varepsilon}{(a/2)a} = \frac{4(K+1)\varepsilon}{a^2}. \tag{10}$$

It follows from (3), (7) and (10) that

$$\left\| \frac{\Phi_\varepsilon(x)}{\|\Phi_\varepsilon(x)\|} - \frac{\Phi_\varepsilon(Ux)}{\|\Phi_\varepsilon(Ux)\|} \right\| > \beta - \frac{8(K+1)\varepsilon}{a^2} > 0,$$

if

$$\varepsilon < \frac{a^2\beta}{8(K+1)}.$$

Using the above mentioned result of Krasnoselsky – Jaworowski we infer that the degree of the mapping $\Phi_\varepsilon(x)/\|\Phi_\varepsilon(x)\|$ is odd. Finally, following Leray – Schauder [6], we can state that the degree of the mapping Φ is odd and thus the theorem is proved.

Theorem 1 implies the following

THEOREM 2. *Let F be a completely continuous operator, defined on the sphere Q without fixed point on the boundary S. If condition* (3) *is satisfied, then F possesses a fixed point in Q, i.e. there exists an element $x_0 \in Q$ such that*

$$F(x_0) = x_0.$$

REMARK. Let us assume that $U(x)=-x$ for $x \in S$, i. e. the involution is replaced by the antipodal mapping. Suppose also that a completely continuous operator F is defined on S and that $\Phi(x)=F(x)-x$ does not vanish on S. In this case the following conditions (A) and (B) are equivalent:

$$\text{(A)} \qquad \inf_{x \in S} \left\| \frac{\Phi(x)}{\|\Phi(x)\|} - \frac{\Phi(-x)}{\|\Phi(-x)\|} \right\| > 0,$$

$$\text{(B)} \qquad \frac{\Phi(x)}{\|\Phi(x)\|} \neq \frac{\Phi(-x)}{\|\Phi(-x)\|} \quad \text{for every} \quad x \in S.$$

Proof. It is sufficient to prove that condition (B) implies condition (A). If our statement were not true, there would exist a sequence of elements $x_n \in S$ $(n=1,2,\ldots)$ such that

$$\text{(11)} \qquad \frac{\Phi(x_n)}{\|\Phi(x_n)\|} - \frac{\Phi(-x_n)}{\|\Phi(-x_n)\|} \to 0 \quad \text{as} \quad n \to \infty.$$

Then

$$\frac{F(x_n)-x_n}{\|F(x_n)-x_n\|} - \frac{F(-x_n)+x_n}{\|F(-x_n)+x_n\|} =$$

$$= \frac{\|F(-x_n)+x_n\|F(x_n)-\|F(x_n)-x_n\|F(-x_n)-(\|F(-x_n)+x_n\|+\|F(x_n)-x_n\|)x_n}{\|F(x_n)-x_n\| \cdot \|F(-x_n)+x_n\|} \to 0,$$

as $n \to \infty$.

Since $F(S)$ is a compact set, we can choose by (2) and (8) a subsequence $\{x_{n_p}\}$ such that all sequences:

$$\{F(x_{n_p})\}, \quad \{F(-x_{n_p})\}, \quad \{\|F(x_{n_p})-x_{n_p}\|\}, \quad \{\|F(-x_{n_p})+x_{n_p}\|\}$$

are convergent. Hence we conclude that the sequence $\{x_{n_p}\}$ converges to some element x_0 of S and, by (11), we obtain $\Phi(x_0)/\|\Phi(x_0)\|=\Phi(-x)/\|\Phi(-x_0)\|$, which contradicts condition (B). We thus obtain the following theorem of Krasnoselsky [3] as a particular case of Theorem 1:

Let F be a completely continuous operator, defined on S, without a fixed point. If condition (B) is fulfilled, then the degree of the mapping $\Phi(x)=F(x)-x$ is odd.

If U is a continuous involution, defined on the boundary S of an n-dimensional Euclidean sphere Q, then condition (3) and the condition $\Phi(x)/\|\Phi(x)\| \neq \Phi(Ux)/\|\Phi(Ux)\|$ for $x \in S$ are, evidently, equivalent.

Thus Theorem 1 is a generalisation to a infinite-dimensional space of the above mentioned result of Krasnoselsky – Jaworowski.

INSTITUTE OF MATHEMATICS, POLISH ACADEMY OF SCIENCES

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MATHEMATICS

On Functions $\varphi(n)$ and $\sigma(n)$

by

A. SCHINZEL

Presented by W. SIERPIŃSKI on June 21, 1955

The object of the present note is to prove the following two theorems:

THEOREM 1. *For every finite sequence of positive numbers $a_1, a_2, \ldots, a_h$ there exists an increasing infinite sequence of natural numbers $n_1, n_2, \ldots$ such that*

$$\lim_{k=\infty} \frac{\varphi(n_k+i)}{\varphi(n_k+i-1)} = a_i \quad \text{for} \quad i=1,2,\ldots,h.$$

THEOREM 2 is obtained from Theorem 1 by replacing the letter φ by σ.

LEMMA 1. *Let $u_n (n=1,2,\ldots)$ denote an infinite sequence of real numbers such that*

$$\lim_{n=\infty} u_n = +\infty, \quad \lim_{n=\infty} \frac{u_{n+1}}{u_n} = 1.$$

Then, for every real number $C>1$ and for every increasing infinite sequence of natural numbers n_k, there exists an infinite sequence of natural numbers l_k such that

$$\lim_{k=\infty} \frac{u_{l_k}}{u_{n_k}} = C.$$

Proof. Let $n_k (k=1,2,\ldots)$ denote a given increasing infinite sequence of natural numbers. For every natural number k let us denote by l_k the least natural number for which

$$\frac{u_{l_k}}{u_{n_k}} > C;$$

such a number exists, since

$$\lim_{l=\infty} u_l = +\infty.$$

Thus we have

$$\frac{u_{l_k}}{u_{n_k}} > C \geqslant \frac{u_{l_k-1}}{u_{n_k}},$$

whence

$$1 > C : \frac{u_{l_k}}{u_{n_k}} \geqslant \frac{u_{l_k-1}}{u_{l_k}}$$

and, in view of

$$\lim_{k=\infty} \frac{u_{l_k-1}}{u_{l_k}} = 1,$$

$$\lim_{k=\infty} \frac{u_{l_k}}{u_{n_k}} = C, \text{ q.e.d.}$$

LEMMA 2. *If g is a natural number, and if $A_0, A_1, \ldots, A_g$ are natural numbers >1 relatively prime in pairs, then there exists a natural number m such that, for $i = 0, 1, \ldots, g$,*

$$A_i \mid m+i, \quad \left(A_i, \frac{m+i}{A_i}\right) = 1, \quad (A_0 A_1 \ldots A_g)^2 > m+i.$$

Proof. In virtue of the so-called Chinese remainder theorem there exists a natural number m_1 such that

$$m_1 + i \equiv A_1 \pmod{A_1^2} \quad \text{for} \quad i = 0, 1, \ldots, g.$$

Let $m = m_1 - A_0^2 A_1^2 \cdot \ldots \cdot A_g^2 E \dfrac{m_1+g}{A_0^2 A_1^2 \cdot \ldots \cdot A_g^2}$. We shall have $A_i \mid m+i$ and $\left(A_i, \dfrac{m+i}{A_i}\right) = 1$, since

$$A_i \mid m_1 + i, \quad \frac{m+i}{A_i} \equiv \frac{m_1+i}{A_i} \equiv 1 \pmod{A_i} \quad \text{for} \quad i = 0, 1, \ldots, g.$$

We shall also have $-g \leqslant m < (A_0 A_1 \ldots A_g)^2 - g$.

If we had $m \leqslant 0$, we should have for $i = -m$, $0 \leqslant i \leqslant g$ and $A_i^2 \mid m+i$, which is impossible, since $A_i > 1$. Thus m is an integer such that for $i = 0, 1, \ldots, g$

$$(A_0 A_1 \ldots A_g)^2 > m+i > 0.$$

LEMMA 3a. *For every finite sequence of real numbers, $b_1, b_2, \ldots, b_g$, satisfying the inequality*

$$\frac{\varphi(i)}{i} > b_i > 0 \quad \text{for} \quad i = 1, 2, \ldots, g,$$

there exists a sequence m_k such that

$$\lim_{k\to\infty}\frac{\varphi(m_k+i)}{m_k+i}=b_i, \qquad i=1,2,\dots,g.$$

Proof. Assume in Lemma 1 that

$$u_n=\prod_{i=1}^{n}\left(\frac{1}{1-\frac{1}{p_i}}\right)$$

(where p_i is the i-th prime number) and that

$$C_i=\frac{1}{b_i}\frac{\varphi(i)}{i},$$

and for $k\geqslant g$, $i=1,2,\dots,g$, let

$$A_{0,k}=g!p_1\cdot p_2\cdot\dots\cdot p_k, \qquad A_{i,k}=p_{l_{i-1,k}+1}\cdot\dots\cdot p_{l_{i,k}},$$

where $l_{0,k}=k$ and $l_{i,k}$ is the number l_k from Lemma 1 suitably chosen for the number C_i and the sequence $l_{i-1,k}$.

In virtue of Lemma 2 there exists a number m_k such that

$$A_{i,k}\mid m_k+i,\ \left(\frac{m_k+i}{A_{i,k}},\ A_{i,k}\right)=1,\ (A_{0,k}A_{1,k}\dots A_{g,k})^2>m_k+i>0$$

for $i=0,1,\dots,g$.

Moreover, for $i,j>0$

(1) $$(A_{0,k},m_k+i)=(A_{0,k},i)=i$$

(2) $$\left(p_1p_2\cdot\dots\cdot p_k,\frac{m_k+i}{i}\right)\Big|\left(\frac{A_{i,k}}{i},\frac{m_k+i}{i}\right)=1$$

(3) $$(A_{j,k},m_k+i)=(A_{j,k},i-j)=1$$

for $i\neq j$, because $k\geqslant g$.

Accordingly, for $i=1,2,\dots,g$,

$$m_k+i=iA_{i,k}q_{i,1}^{\alpha_{i,1}}q_{i,2}^{\alpha_{i,2}}\dots q_{i,s_i}^{\alpha_{i,s_i}},$$

where

$$p_{l_{g,k}}<q_{i,1}<q_{i,2}<\dots<q_{i,s_i}$$

are prime numbers and, of course, $s_i<2l_{g,k}$. Hence,

$$\frac{\varphi(i)}{i}\cdot\frac{\varphi(A_{i,k})}{A_{i,k}}>\frac{\varphi(m_k+i)}{m_k+i}=\frac{\varphi(i)}{i}\cdot\frac{\varphi(A_{i,k})}{A_{i,k}}\cdot\prod_{j=1}^{s_i}\left(1-\frac{1}{q_{i,j}}\right)>$$

$$>\frac{\varphi(i)}{i}\cdot\frac{\varphi(A_{i,k})}{A_{i,k}}\cdot\prod_{j=1}^{s_i}\left(1-\frac{1}{p_{l_{g,k}}+j}\right)>\frac{\varphi(i)}{i}\cdot\frac{\varphi(A_{i,k})}{A_{i,k}}\cdot\frac{p_{l_{g,k}}}{p_{l_{g,k}}+2l_{g,k}}.$$

and, in virtue of the formulas

$$\lim_{k\to\infty}\frac{u_{l_{i-1,k}}}{u_{l_{i,k}}}=b_i\cdot\frac{i}{\varphi(i)},\qquad \lim_{k\to\infty}\frac{p_{l_{g,k}}}{p_{l_{g,k}+2l_{g,k}}}=1,$$

we have

$$\lim_{k=\infty}\frac{\varphi(m_k+i)}{m_k+i}=b_i.$$

LEMMA 3b. *For every finite sequence of real numbers, $b_1,b_2,\dots,b_g$ satisfying the inequality*

$$b_i>\frac{\sigma(i)}{i}\qquad \textit{for}\qquad i=1,2,\dots,g,$$

there exists a sequence m_k, such that

$$\lim_{k\to\infty}\frac{\sigma(m_k+i)}{m_k+i}=b_i,\qquad i=1,2,\dots,g.$$

Proof. Assume in Lemma 1 that

$$u_n=\prod_{i=1}^{n}\left(1+\frac{1}{p_i}\right)$$

(where p_i is the i-th prime number) and that $C_i=b_i\cdot i/\sigma(i)$, and, for $k\geqslant g$, $i=1,2,\dots,g$, let

$$A_{0,k}=g!p_1\cdot p_2\cdot\dots\cdot p_k,\qquad A_{i,k}=p_{l_{i-1,k}+1}\cdot\dots\cdot p_{l_{i,k}},$$

where $l_{i,k}$ are the numbers from Lemma 1 (on the whole different from those in Lemma 3a).

Analogically to the proof of Lemma 3a, we prove the existence of a number m_k such that, for $i=1,2,\dots,g$,

$$m_k+i=iA_{i,k}q_{i,1}^{a_{i,1}}q_{i,2}^{a_{i,2}}\cdot\dots\cdot q_{i,s_i}^{a_{i,s_i}},$$

where

$$p_{l_{g,k}}<q_{i,1}<\dots<q_{i,s_i}$$

are prime numbers (on the whole different from those in Lemma 3a) and $s_i<2l_{g,k}$. Hence,

$$\frac{\sigma(i)}{i}\cdot\frac{\sigma(A_{i,k})}{A_{i,k}}<\frac{\sigma(m_k+i)}{m_k+i}<\frac{\sigma(i)}{i}\frac{\sigma(A_{i,k})}{A_{i,k}}\cdot\prod_{j=1}^{s_i}\left(\frac{q_{i,j}}{q_{i,j}-1}\right)<$$

$$<\frac{\sigma(i)}{i}\frac{\sigma(A_{i,k})}{A_{i,k}}\cdot\prod_{j=1}^{s_i}\frac{p_{l_{g,k}}+j}{p_{l_{g,k}}+j-1}<\frac{\sigma(i)}{i}\frac{\sigma(A_{i,k})}{A_{i,k}}\cdot\frac{p_{l_{g,k}}+2l_{g,k}}{p_{l_{g,k}}},$$

whence, as in Lemma 3a,

$$\lim_{k=\infty}\frac{\sigma(m_k+i)}{m_k+i}=\frac{\sigma(i)}{i}\cdot\lim_{k\to\infty}\frac{\sigma(A_{i,k})}{A_{i,k}}=b_i,\qquad \text{q.e.d.}$$

REMARK. In the case of $g=1$ lemmas 3a and 3b imply W. Sierpiński's theorems on the density of the sets

$$\left\{\frac{\varphi(m)}{m}\right\}_{m=1,2,\ldots} \quad \text{in} \quad [0,1] \quad \text{and} \quad \left\{\frac{\sigma(m)}{m}\right\}_{m=1,2,\ldots} \quad \text{in} \quad [1,\infty],$$

Proof of Theorem 1. Assume in Lemma 3a that $g=h+1$ and that $b_{1+i}=b_1a_1\cdot\ldots\cdot a_i$ $(i=1,\ldots,h)$, where b_1 is so small that

$$b_{1+i}<\frac{\varphi(i+1)}{i+1}, \quad \text{for} \quad i=0,1,\ldots,h.$$

Thus there exists a sequence n_k such that

$$\lim_{k\to\infty}\frac{\varphi(n_k+i)}{n_k+i}=b_{1+i} \quad \text{for} \quad i=0,1,\ldots,h.$$

Hence

$$\lim_{k\to\infty}\frac{\varphi(n_k+i)}{\varphi(n_k+i-1)}=\frac{b_{1+i}}{b_i}=a_i \quad \text{for} \quad i=1,\ldots,h, \quad \text{q.e.d.}$$

I have been informed that the proof of this theorem, based on Brun's method, has also been given by Y. Wang; the proof has not yet appeared in print.

The proof of Theorem 2 is analogous to the preceding one but based on Lemma 3b.

CONCLUSIONS. In Theorems 1 and 2 we can, of course, take 0 or ∞ for a_i $(i=1,2,\ldots,h)$.

REMARK. Setting $h=1$ in Theorems 1 and 2 we obtain the theorems on the density of sets

$$\left\{\frac{\varphi(n+1)}{\varphi(n)}\right\}_{n=1,2,\ldots} \quad \text{and} \quad \left\{\frac{\sigma(n+1)}{\sigma(n)}\right\}_{n=1,2,\ldots} \quad \text{in} \quad [0,\infty]\ [1].$$

Setting $h=2$, $a_1=\infty$, $a_2=0$; $a_1=0$, $a_2=\infty$; $a_1=\infty$, $a_2=\infty$; $a_1=0$, $a_2=0$, we obtain a theorem from W. Sierpiński's and my note [2]; setting $a_1=a_2=\ldots=a_h=\infty$ and $a_1=a_2=\ldots=a_h=0$, we obtain a theorem from another note of mine [3].

The case of $h=1$, $a_1=\infty$ and $a_1=0$ gives a theorem of B.S.K.R. Somayajulu [4].

INSTITUTE OF MATHEMATICS, POLISH ACADEMY OF SCIENCES, WARSAW

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MATHEMATICS

Note on the General Theory of Closed Continuous Mappings of Bicompact T_1 Spaces

by

W. SŁOWIKOWSKI

Presented by K. KURATOWSKI on June 29, 1955

In this paper I wish to present an algebraic point of view on the theory of closed continuous mappings of bicompact T_1 spaces. In this way I obtain the natural characterisation of the family of inverse images of an arbitrary closed continuous mapping of bicompact T_1 spaces.

This result may be applied to the theory of semicontinuous decompositions of bicompact T_1 spaces. The algebraic object under consideration I shall name a Γ-algebra. A set $\mathfrak{A}$ is a *Γ-algebra* if:

α. The operations of addition and multiplication defined in $\mathfrak{A}$ are both commutative and associative,

β. $A(B+C)=AB+AC$ for every $A,B,C \in \mathfrak{A}$,

γ. There exist in $\mathfrak{A}$ elements 1 and 0 such that $1A=A=0+A$; $1+A=1$; $0A=0$ for every A,

δ. $A=B$ if, and only if, $A+B+C=1$ implies $AB+C=1$ for every $C \in \mathfrak{A}$.

It is easy to see that if a basis $\mathfrak{A}$ of open sets in a bicompact T_1-space is multiplicative and additive, then it is a Γ-algebra. Conversely, it has been proved in [2] that if we introduce the topology in the space $\mathfrak{M}(\mathfrak{A})$ of all maximal ideals of an arbitrary Γ-algebra $\mathfrak{A}$ in such a way that the sets

$$\Gamma_A = \underset{M \in \mathfrak{M}(\mathfrak{A})}{F} (A \bar{\in} M),$$

where $A \in \mathfrak{A}$ form the basis, then $\mathfrak{M}(\mathfrak{A})$ is a bicompact T_1-space and the mapping $f(A)=\Gamma_A$ is an isomorphism of the Γ-algebra $\mathfrak{A}$ onto a multiplicative and additive basis of open subsets of $\mathfrak{M}(\mathfrak{A})$.

The following properties have been proved in [2]:

1. *If an algebra $\mathfrak{A}$ satisfies axioms α. β. and γ. then for every $M \in \mathfrak{M}(\mathfrak{A})$ and $A, B \in \mathfrak{A}$*

$$A+B \bar{\in} M \quad \text{if, and only if,} \quad A \bar{\in} M \quad \text{or} \quad B \bar{\in} M$$

$$AB \bar{\in} M \quad \text{if, and only if,} \quad A \bar{\in} M \quad \text{and} \quad B \bar{\in} M.$$

2. *An algebra $\mathfrak{A}$ satisfying axioms α. β. and γ. is a Γ-algebra if, and only if, the following condition is fulfilled:*

If, for every $M \in \mathfrak{M}(\mathfrak{A})$, $AB \in M$ implies $A+B \in M$, then $A=B$.

3. *Let $\mathfrak{A}_0$ be a subalgebra of a Γ-algebra $\mathfrak{A}$. Every maximal ideal of $\mathfrak{A}_0$ may be extended to a maximal ideal of $\mathfrak{A}$.*

Let $\mathfrak{A}_0$ be a subalgebra of a Γ-algebra $\mathfrak{A}$. We consider the two following conditions:

(a) $M \in \mathfrak{M}(\mathfrak{A})$ implies $M \cap \mathfrak{A}_0 \in \mathfrak{M}(\mathfrak{A}_0)$,

(a′) the set $\underset{M \cap \mathfrak{A}_0}{F'} (I \subset M \in \mathfrak{M}(\mathfrak{A}))$, where I is an arbitrary ideal of $\mathfrak{A}$, is closed in $\mathfrak{M}(\mathfrak{A}_0)$.

Every subalgebra $\mathfrak{A}_0$ of Γ-algebra $\mathfrak{A}$ satisfying condition (a) is a Γ algebra since $\mathfrak{A}_0$ has property 2. It is easy to see that if $\mathfrak{A}_0$ satisfies condition (a), then the mapping $f(M)=M \cap \mathfrak{A}_0$ is a continuous mapping of $\mathfrak{M}(\mathfrak{A})$ onto $\mathfrak{M}(\mathfrak{A}_0)$. The continuity of f is an evident consequence of the equality

$$f^{-1}\Big(\underset{M \in \mathfrak{M}(\mathfrak{A}_0)}{F'} (A \bar{\in} M)\Big) = \underset{N \in \mathfrak{M}(\mathfrak{A})}{F'} (A \bar{\in} N).$$

The mapping f is closed (i. e. maps closed sets onto closed sets) if, and only if, $\mathfrak{A}_0$ also satisfies condition (a′). Conversely, let f be a continuous mapping of a bicompact T_1 space $\boldsymbol{X}$ onto a bicompact T_1 space $\boldsymbol{Y}$. If $\mathfrak{A}$ is a multiplicative and additive basis of $\boldsymbol{X}$ and $\mathfrak{A}_0 \subset \mathfrak{A}$ is the family of inverse images of the sets of multiplicative and additive basis $\mathfrak{A}'$ of $\boldsymbol{Y}$ then $\mathfrak{A}_0$ satisfies condition (a). In fact, it is well known that the transformations:

$$M(t)=\Big(\underset{A \in \mathfrak{A}}{F'} (t \in A)\Big) \in \mathfrak{M}(\mathfrak{A}), \qquad M'(t)=\Big(\underset{A \in \mathfrak{A}'}{F'^{1}} (\tau \bar{\in} A)\Big) \in \mathfrak{M}(\mathfrak{A}')$$

and

$$M_0(t)=\Big(\underset{f^{-1}(A)}{F} (\tau \bar{\in} A \in \mathfrak{A}')\Big) \in \mathfrak{M}(\mathfrak{A}_0)$$

are homeomorphisms of $\boldsymbol{X}$ onto $\mathfrak{M}(\mathfrak{A})$, of $\boldsymbol{Y}$ onto $\mathfrak{M}(\mathfrak{A}')$, and of $\boldsymbol{Y}$ onto $\mathfrak{M}(\mathfrak{A}_0)$, respectively.

The ideal $M(t) \cap \mathfrak{A}_0$ is maximal since $M(t) \cap \mathfrak{A}_0 = M_0(f(t)) \in \mathfrak{M}(\mathfrak{A}_0)$.

If the mapping f is closed, then the set $f(\boldsymbol{X}-A)$ is closed for every $A \in \mathfrak{A}$. Hence the set $M_0(f(\boldsymbol{X}-A))$ is also closed. The equality

$$\underset{M \cap \mathfrak{A}_0}{F'} (M \supset I) = \prod_{A \in I} M_0(f(\boldsymbol{X}-A))$$

shows that condition (a′) is fulfilled.

We shall say that $\mathfrak{A}_0$ *induces the image of* $\mathfrak{M}(\mathfrak{A})$ if $\mathfrak{A}_0$ satisfies condition (a). If $\mathfrak{A}_0$ also satisfies condition (a'), then we shall say that $\mathfrak{A}_0$ *induces the closed image of* $\mathfrak{M}(\mathfrak{A})$.

Now I shall prove the following fundamental

THEOREM. *Let* $\mathfrak{A}$ *be a* Γ*-algebra. A subalgebra* $\mathfrak{A}_0 \subset \mathfrak{A}$ *induces the closed image of* $\mathfrak{M}(\mathfrak{A})$ *if, and only if, the following condition is fulfilled*:

(b) *for arbitrary elements* $A \in \mathfrak{A}_0$ *and* $Z \in \mathfrak{A}$ *such that* $A+Z=1$, *there exists an element* $B \in \mathfrak{A}_0$ *such that* $A+B=1$ *and* $BZ=B$.

Proof. *Necessity.* Suppose condition (a) is satisfied and (b) is not satisfied. Then there are elements $Z \in \mathfrak{A}$ and $A \in \mathfrak{A}_0$ such that $BZ=B \in \mathfrak{A}_0$ implies $A+B \neq 1$. The set

$$I = \underset{B+AC}{E}(B, C \in \mathfrak{A}_0)(BZ=B)$$

is an ideal of $\mathfrak{A}_0$. Let $M_0 \subset \mathfrak{A}_0$ be a maximal ideal containing the ideal I. The element Z does not belong to an extension of M_0 to a maximal ideal of $\mathfrak{A}$. This means that M_0 is not contained in the set $\Delta = \underset{M \cap \mathfrak{A}_0}{E}(Z \in M \in \mathfrak{M}(\mathfrak{A}_0))$. Further, if $M_0 \in \Gamma_B = \underset{M \in \mathfrak{M}(\mathfrak{A}_0)}{E}(B \in M)$, where $B \in \mathfrak{A}_0$, then $B \in M_0$, which implies $BZ \neq B$. Hence there is an ideal M such that $Z \in M$ and $B \bar{\in} M$. This means that if $M_0 \in \Gamma_B$, then $\Gamma_B \cap \Delta \neq 0$. Therefore $M_0 \in \bar{\Delta} - \Delta$, where $\bar{\Delta}$ is the closure of Δ in $\mathfrak{M}(\mathfrak{A})_0$. Hence Δ is not closed.

Sufficiency. If $M \in \mathfrak{M}(\mathfrak{A})$ and $A \in \mathfrak{A}_0 - M$, then there is an element $Z \in M$ such that $A+Z=1$. By condition (b) there is an element $B \in \mathfrak{A}_0$ such that $A+B=1$ and $BZ=B \in M$ Then the element $A \in \mathfrak{A}_0$ does not belong to any extension of the ideal $M \cap \mathfrak{A}_0$ to a maximal ideal in $\mathfrak{A}_0$. Hence $M \cap \mathfrak{A}_0$ is maximal in $\mathfrak{A}_0$.

Let I be a certain ideal of $\mathfrak{A}$ and let $\Delta = \underset{M \cap \mathfrak{A}_0}{E}(I \subset M)$. If $M_0 \in \mathfrak{M}(\mathfrak{A}_0) - \Delta$, then no extension of M_0 to a maximal ideal of $\mathfrak{A}$ contains the ideal I. Therefore we may choose the elements $A \in M_0$ and $Z \in I$ such that $A+Z=1$. By condition (b) there exists $B \in \mathfrak{A}_0$ such that $A+B=1$ and $BZ=B \in I$. Hence for every ideal $M_0 \in \mathfrak{M}(\mathfrak{A}_0) - \Delta$ there exists a neighbourhood of M_0 which is disjoint with Δ. Therefore Δ is closed.

REMARK 1. *Let* $\mathfrak{A}$ *be a* Γ*-algebra. If an additive family* $\mathfrak{R}$ *of elements of* $\mathfrak{A}$ *satisfies condition* (b), *then the subalgebra* $\mathfrak{A}_0 \subset \mathfrak{A}$ *generated by* $\mathfrak{R}$ *also satisfies condition* (b).

$\mathfrak{A}_0$ consists of elements of the form $A_1 A_2 \dots A_k$, where $A_1, A_2, \dots, A_k \in \mathfrak{R}$. For every $Z \in \mathfrak{A}$ and $A_1, A_2, \dots, A_k \in \mathfrak{R}$ we have $Z + A_1 A_2 \dots A_k = 1$ if, and only if, $Z + A_i = 1$ for $i = 1, 2, \dots, k$. If $B_i \in \mathfrak{R}$ are such that $B_i Z = B$ and $A_i + B_i = 1$, then

$$(A_1+B_1)(A_2+B_2) - (A_k+B_k) = A_1 A_2 \dots A_k + C = 1,$$

where $CZ = C \in \mathfrak{A}_0$.

REMARK 2. *If the space* $\mathfrak{M}(\mathfrak{A}_0)$ *is normal (i. e. if for every* $A,B \in \mathfrak{A}_0$ *such that* $A+B=1$, *there exists such* $U,V \in \mathfrak{A}_0$ *that* $UV=0$ *and* $U+A=V+B=1$), *then condition* (a) *implies condition* (a'), *since then the mapping* $f(M)=M\cap\mathfrak{A}_0$ *is closed. Further if, the* Γ*-algebra* $\mathfrak{A}$ *is normal, then every subalgebra satisfying condition* (b) *is also normal. Hence, for normal* Γ*-algebras, conditions* (a) *and* (b) *are equivalent.*

Let $\mathfrak{A}_0$ be a certain subalgebra of Γ-algebra $\mathfrak{A}$ satisfying condition (b). The family of sets

$$F_N=\underset{M\in\mathfrak{M}(\mathfrak{A})}{E}(M\supset N\in\mathfrak{M}(\mathfrak{A}_0))$$

forms a semicontinuous decomposition of the space $\mathfrak{M}(\mathfrak{A})$ (see [1]). The image induced by this decomposition is obviously $\mathfrak{M}(\mathfrak{A}_0)$ and $f(M)=M\cap\mathfrak{A}_0$ is the mapping of $\mathfrak{M}(\mathfrak{A})$ onto $\mathfrak{M}(\mathfrak{A}_0)$ induced by this decomposition.

Conversely, let $\boldsymbol{X}$ be a T_1 bicompact space and let a family Φ of closed sets of $\boldsymbol{X}$ establish a semicontinuous decomposition of $\boldsymbol{X}$. We denote by $\mathfrak{A}$ the family of all open sets of $\boldsymbol{X}$ and by $\mathfrak{A}_0$ the family of open sets of the form $A_Z=\prod_{(X-F)+Z\neq X}(X-F)$ where $F\in\Phi$ and Z is an arbitrary element of $\mathfrak{A}$.

If $Z'+A_Z=X=1$, then $A_Z+A_{Z'}=X=1$ and $A_{Z'}Z'=A_{Z'}$. Therefore $\mathfrak{A}_0$ induces the closed image of $\mathfrak{M}(\mathfrak{A})\overset{\text{top}}{=}\boldsymbol{X}$. The space $\mathfrak{M}(\mathfrak{A}_0)$ is topologically identical with the space $\{\Phi\}$ induced by Φ [1].

I wish to thank Professor Kuratowski for his valuable suggestions and help during the preparation of this note.

INSTITUTE OF MATHEMATICS, POLISH ACADEMY OF SCIENCES

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EXPERIMENTAL PHYSICS

The Influence of X-Radiation on the Electrical Conductivity of Photosensitive PbS and Tl_2S Layers

by

B. BURAS and A. ZARĘBA

Presented by A. SOŁTAN on June 10, 1955

Introduction

It is known that in specially sensitised microcrystalline layers of lead sulphide and thallous sulphide, electrical conductivity shows a marked dependence on the intensity of illumination, both in the visual and in the infra-red part of the spectrum. For constant illumination the measure of the light sensitivity of the layer is given by

$$S = \frac{\Delta\sigma}{\sigma},$$

where σ is the dark conductivity and $\Delta\sigma$ the change in conductivity produced by illumination of the layer. The aim of the present work was to investigate whether a change in conductivity is produced by X-radiation and whether a correlation exists between sensitivity to visible and infra-red radiation and sensitivity to X-radiation.

Apparatus and methods of measurement

Microcrystalline layers of PbS and Tl_2S, of a thickness of the order of a micron were used for the investigations. These layers were produced by evaporation *in vacuo* and were resublimed on the inside surface of the flat wall of a glass envelope [1], [2]. The pressure in the envelope at the moment of sealing off on the vacuum line was of the order of 10^{-6} mm. Hg. Two tungsten electrodes were sealed in the envelope and connected to the evaporated film by graphite strips painted on the glass.

The source of X-rays was a glass Coolidge tube with a tungsten anode, powered by a rectified and smoothed high voltage supply of 60 kV.

A constant electron current of 6 mA was used, and the unfiltered X-ray beam was modulated at a frequency of 730 c/s by means of a 2 mm. thick rotating brass disk provided with circular holes. The radiation was directed through a thin aluminium foil on to a semiconductor cell which was enclosed in an earthed shield placed at a distance of about 15 cm. from the focus of the X-ray tube. The electrical impulses in the cell circuit were amplified 130,000 times by a tuned amplifier and measured by a voltmeter (Fig. 1).

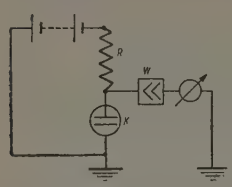

Fig. 1.
K – The layer investigated
R – Load resistance
W – Amplifying unit

In order to take measurements at low temperatures, the cell was cooled by a stream of cold air evaporated from liquid air. The temperature was measured by a thermocouple attached to the outside of the cell. Temperatures down to −80°C. were obtained.

Results

It was found that some of the microcrystalline films of PbS and Tl_2S changed their electrical conductivity under the influence of X-radiation. This change is to be observed when a certain threshold voltage has been

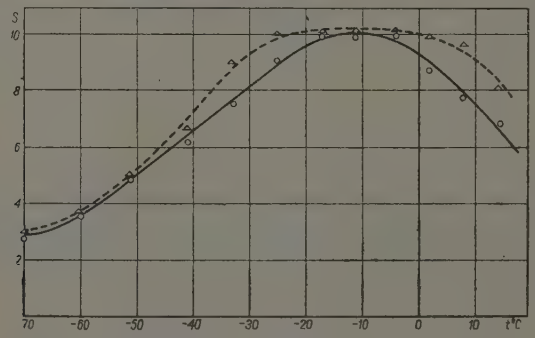

Fig. 2. X-ray sensitivity in arbitrary units (dotted line)
Optical sensitivity in arbitrary units (continuous line)

exceeded in the X-ray tube. This threshold voltage, which is common to all X-ray sensitive layers, is connected with the absorption of the rays by the glass—both of the X-ray tube and of the envelope in which the layer is situated. At a tube voltage of 55 kV and a tube current of 6 mA, the observed voltage signal at the cell was of an amplitude of an order greater than the noise level.

In order to determine whether the observed effect is the direct result of the action of X-rays on the microcrystalline film, a series of control

measurements were taken which confirmed that we were dealing with a direct action and not with an indirect effect caused, for example, by fluorescence of the glass envelope.

In order to determine whether a correlation exists between X-ray and light sensitivity, 6 PbS and 10 Tl_2S layers were studied, using for the layers of the semiconductor a constant light source and identical conditions of X-radiation. It appears that for layers of low light-sensitivity the X-ray sensitivity is not measurable; layers of high light-sensitivity, on the other hand, show noticeable X-ray sensitivity.

For the purpose of studying further this correlation, measurements were taken of the dependence on temperature of light and X-ray sensitivities at temperatures ranging between -80°C. and $+20^{\circ}$C. The results of these measurements for one particular layer are shown in Fig. 2. Bearing in mind the fact that within this temperature range, the resistance of the layer changes 20 times whereas its sensitivity changes only several times, the similarity between the change in the two sensitivities is quite remarkable.

Conclusions

By means of the photo-electric and Compton effects, X-rays can raise electrons to the conducting band from lower energy levels than can light and infra-red rays. On the basis of the concentration theory it would be more difficult to explain the analogous effect of sensitisation on sensitivity to light and X-rays. If, on the other hand, the barrier theory is correct, the effect of the barrier formed in the process of production of the layer should be the same for all electrons, no matter from what energy level they come, and the observed parallelism in different parts of the spectrum should occur. The results given here would seem to constitute one more argument in favour of the barrier theory of photoconductivity.

The authors are indebted to the late Professor S. Pieńkowski for making possible and encouraging this work and also to Professor L. Sosnowski for stimulating discussion.

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INSTITUTE OF PHYSICS, POLISH ACADEMY OF SCIENCES

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CHEMISTRY

Peroxycomplexes as Intermediate States in the Electron Transfer Reaction

by

B. JEŻOWSKA-TRZEBIATOWSKA and H. PRZYWARSKA

Communicated by W. TRZEBIATOWSKI at the meeting of May 16, 1955

In oxidation-reduction processes intermediate states are possible. These may consist in the formation by the oxidising agent and the reductant of a complex compound in which a preliminary shift of the electron cloud towards the atom of the oxidising agent takes place. This shift depends upon the electro-negativity of the oxidising atom.

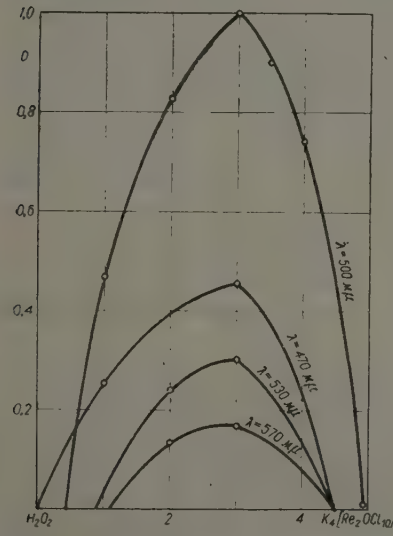

Fig. 1. Optical density curve according to the Job method. Initial concentrations of equimolar solutions of H_2O_2 and $K_4[Re_2OCl_{10}]$ – $1.16 \cdot 10^{-2}$M/l

The action of H_2O_2 as an oxidising agent on a binuclear complex $K_4[Re_2O\ Cl_{10}]$ forms the subject of this paper. Preliminary work [1] has shown that acid solutions of $K_2[Re\ Cl_5OH]$ undergo oxidation directly to perrhenate, whereas μ-oxychlororhenate (IV) passes through an intermediate oxidation state forming a blood-red solution. This colour disappears slowly, because of the formation of colourless perrhenate.

The formation of an intermediate red compound was investigated by Job's method of continuous variations [2]–[4], using a photometer of the Pulffrich type with suitable filters and a solution layer of 5 mm. In the μ-oxychlororhenate – H_2O_2 system the maximum of the curve (Fig. 1) occurs at a 1:3 components ratio. On the curves obtained with various wave-lengths the maximum occurs

at the same composition of the mixture. Therefore these absorption curves show that only one coloured complex exists in the solution. The above conclusions were confirmed by the application of optical density measurements of mixtures containing constant amounts of H_2O_2 ($1.04 \cdot 10^{-5}$ M) at varying concentrations of μ-oxychlororhenate (IV) (from $1.59 \cdot 10^{-5}$ to $9.48 \cdot 10^{-5}$ M) (pH = const.).

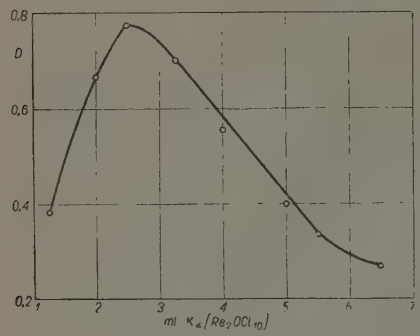

Fig. 2. Optical density curve with varying amounts of $K_4[Re_2OCl_{10}]$ per 9 ml. H_2O_2 solution. Initial concentrations of equimolar solutions of H_2O_2 and $K_4[Re_2OCl_{10}]$—$5.44 \cdot 10^{-3}$ M/l. Wave length: 500 mμ

The maximum of the photometric titration curve corresponds to the molar components 1:3 (Fig. 2).

The further increase in the μ-oxychlororhenate/H_2O_2 ratio caused a gradual decrease in the optical density. This fact suggests that the coloured complex reacts with the excess of μ-oxychlororhenate undergoing decomposition. At a constant concentration of μ-oxychlororhenate ($1.09 \cdot 10^{-5}$ M) and varying concentrations of H_2O_2 (from $1.09 \cdot 10^{-5}$ to $4.35 \cdot 10^{-5}$ M) the optical density of the solution attains a constant value also when the reagents ratio is 1:3. (Fig. 3). This value does not change with a further addition of H_2O_2 and corresponds practically to the complete binding of μ-oxychlororhenate.

These results suggest that the complex μ-oxychlororhenate-$3H_2O_2$ exists in solution.

The complex stability constant was calculated from the optical density values by means of the Babko method [5], [6], and was equal to $K = 1.02 \cdot 10^{14}$. The quinoline and caesium salts were precipitated from the red solution of maximum extinction as reddish-brown crystals. The following analytical results were obtained:

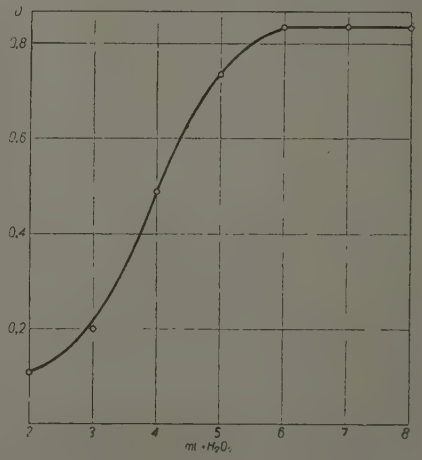

Fig. 3. The optical density curve with varying amounts of H_2O_2 per 2 ml. of $K_4[Re_2OCl_{10}]$. Initial concentrations of equimolar solutions of H_2O_2 and $K_4[Re_2OCl_{10}]$—$5.44 \cdot 10^{-3}$ M/l. Wave length: 500 mμ

Quinoline salt: found: Re—29.42%; Cl—28.4%;
quinoline: —40.0%
calc: Re—29.10%; Cl—28.0%;
quinoline: —40.3%

Caesium salt: found: Re—31.50%; Cl—29.9%; Cs—33.4%
calc.: Re—32.10%; Cl—30.6%; Cs—34.4%

The compositions correspond to the following μ-peroxychlororhenates (quin. $H)_4[Cl_5Re\ O_2\ Re\ Cl_5]$ and $Cs_3H[Cl_5Re\ O_2Re\ Cl_5]$.

The +4 oxidation state of rhenium was established in the following way:

After oxidation with an excess of iron alum, the caesium salt was titrated with permanganate. From the quinoline salt solution, ReO_2 was precipitated and oxidised as above. In both cases it was found that approximately 2 equivalents of permanganate were required per gram-atom of rhenium. But the Re-atom does not indicate the characteristic behaviour of the +5 oxidation state (hydrolysis, oxidability). On the contrary, the complex readily loses the oxygen content and gives reversibly μ-oxychlororhenate (IV). This leads to the conclusion that two bridging oxygen atoms act as oxidising agents. This is supported by the fact that the solution of μ-oxychlororhenate with H_2O_2 (in mol. ratio 1:3) requires at maximum extinction approximately 6 equivalents of $KMnO_4$ per 1 gram-atom of rhenium.

The peroxy-salts dissolved in acid give the same characteristic red solutions. Diminishing the acidity ($pH > 2.2$) changes the colour into yellow. This reaction is reversible and may be related to the equilibrium

$$\underset{\text{yellow}}{[Re_2O_2Cl_{10}]^{4-}} + 4H^+ \rightleftharpoons \underset{\text{red}}{H_4[Re_2O_2Cl_{10}]}.$$

The solid salts and their acid solutions undergo slow decomposition giving μ-oxychlorohenate (IV):

$$[Re_2O_2Cl_{10}]^{4-} \rightarrow [Re_2OCl_{10}]^{4-} + O,$$

and simultaneously there takes place an auto-oxidation-reduction process in which the oxygen atom acts as oxidising agent and rhenium atoms as reducing agent. Therefore rhenium is partially oxidized.

Magnetic susceptibility measurements of the quinoline salt showed its paramagnetism corresponding to the effective moment of 3.5 M.B. The $K_4[Cl_5ReOReCl_5]$ is diamagnetic [7] as a result of spincoupling between paramagnetic rhenium nuclei. The moment indicates a less spin coupling in consequence of an increased distance of two rhenium atoms through the peroxide linkage.

In view of the experiments in solution it is clear that primarily the complex of μ-oxychlororhenate with 3 molecules of H_2O_2 is formed:

$$H_4[Re_2OCl_{10}] + 3H_2O_2 \rightarrow H_4[Re_2O_2Cl_{10}] \cdot 2H_2O_2 + H_2O.$$

Two molecules of H_2O_2 can be joined by hydrogen lingage with oxygen atoms of peroxide bridge. In the crystalline salt, however, there exists only one peroxide-bridge which slowly absorbs the electrons $\overset{-}{\text{Re}}\ldots\overset{\downarrow}{\text{O}}..\overset{\downarrow}{\text{O}}\ldots\text{Re}$, and therefore causes an increase of the oxidation state of the rhenium. The rôle of the bridging atoms is presumably the same for the complexes in solution. In this manner the investigation presented indicates the establishing of the peroxy-complexes as the intermediate stage in the electron transfer process.

LABORATORY OF SOLID STATE CHEMISTRY, POLISH ACADEMY OF SCIENCES
DEPARTMENT OF INORGANIC CHEMISTRY, INSTITUTE OF TECHNOLOGY,
BOLESŁAW BIERUT UNIVERSITY, WROCŁAW

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CHEMISTRY

On the Reaction of 5-Nitro-1,3-dioxane with Diazocompounds, and the Synthesis of Arylazonitrodiols

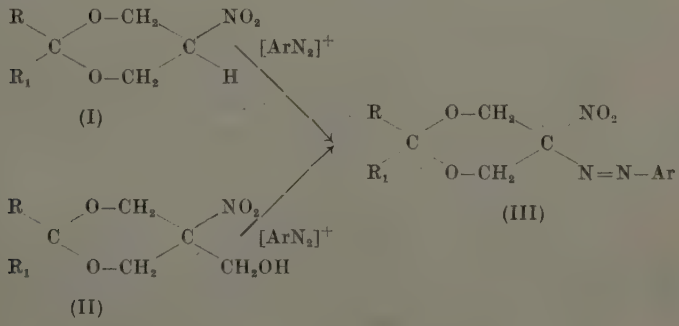
by

Z. ECKSTEIN and T. URBAŃSKI

Communicated by T. URBAŃSKI at the meeting of May 16, 1955

The authors of the present paper continued their experiments, described earlier [1], [2], on the reactivity of derivatives of 5-nitro-1,3-dioxane (I) and of 5-hydroxymethyl-5-nitro-1,3-dioxane (II). They now investigated the formation of azoproducts, through the reaction of the appropriate diazocompounds with the above-mentioned substances.

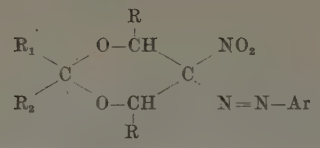
It was established that both compounds (I) and (II) were able to form azoderivatives, when the *pH* was kept between 7.5-8.5, by means of KOH. Prior to the formation of the azocompound, substance (II) lost a molecule of formaldehyde and the azocompounds deriving from (II) were identical with those formed from (I):

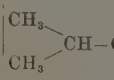


The fact of the formation of azoderivatives from secondary nitrocompounds was already known and had formed the subject matter of a number of publications [3]-[10].

All compounds (III) are coloured in various shades from yellow to red. Their m.ps. are tabulated below (Table I):

TABLE I



Comp. No.	R	R_1	R_2	Ar	M. p. (°C)	Yield per cent
1.	H	H	C_6H_5	C_6H_5	107–108.5	59.1
2a.	H	H	C_6H_5	C_6H_4–Cl–*p*	111.5–113	21.6
2b.					165–167 (d)	7.2
3.	H	H	C_6H_5	C_6H_4–NO_2–*p*	146–148 (d)	27.8
4.	H	H	C_6H_5	C_6H_4–CH_3–*p*	125.5–127	58.2
5a.	H	H	C_6H_5	$C_{10}H_7$–β	126.5–128	18.2
5b.					182–183 (d)	5.6
6.	CH_3	H	C_6H_5	C_6H_5	145–146	49.9
7.	CH_3	H	C_6H_5	C_6H_4–Cl–*p*	155.5–156.5	66.4
8.	CH_3	H	C_6H_5	C_6H_4–NO_2–*p*	186–187 (d)	52.4
9.	CH_3	H	C_6H_5	C_6H_4–CH_3–*p*	141–142	21.1
10.	CH_3	H	C_6H_5	$C_{10}H_7$–β	142–143	31.9
11.	CH_3	H	C_6H_4–Cl–p	C_6H_4–NO_2–*p*	187–188 (d)	28.0
12.	$CH_3CH_2CH_2$	H	C_6H_5	C_6H_4–NO_2–*p*	137–138.5	63.4
13.		H	C_6H_5	C_6H_4–NO_2–*p*	127.5–128.5	18.5
14.	CH_3	CH_3	CH_3	C_6H_5	99–100.5	20.5
15.	CH_3	CH_3	CH_3	C_6H_4–Cl–*p*	138.5–140	38.1
16a.	CH_3	CH_3	CH_3	C_6H_4–NO_2–*p*	120–121	11.7
16b.					163–164 (d)	29.6
17.	CH_3	CH_3	CH_3	$C_{10}H_7$–β	112–114	21.0
18.	H	CH_3	CH_3	C_6H_5	94–95	86.8
19.	H	CH_3	CH_3	C_6H_4–Cl–*p*	142–143.5 (d)	91.8
20.	H	CH_3	CH_3	C_6H_4–NO_2–*p*	173–174 (d)	72.5
21.	H	CH_3	CH_3	C_6H_4–CH_3–*p*	124.5–126	91.2
22.	H	CH_3	CH_3	$C_{10}H_7$–β	133–134	86.4
23.	H	CH_3	CH_3	$C_6H_4SC_6H_4$–NO_2–*p*	168–169 (d)	73.5

(d) Melting points with decomposition.

We were able, by fractional crystallisation, to separate the products into two isomers, *a* and *b*, which differ in their crystalline form, colour, solubility and melting points. When hydrolised, they form the same arylazonitrodiols (IV). They give the same ultraviolet absorption spectra (Table II, and Figs. 1. 2). We suggest that the isomers possess *cis-trans* configuration.

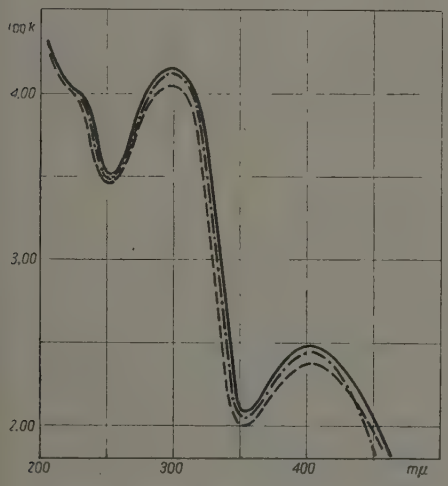


Fig. 1. 2*a* —, 2*b* – – –, 2*c* – · –

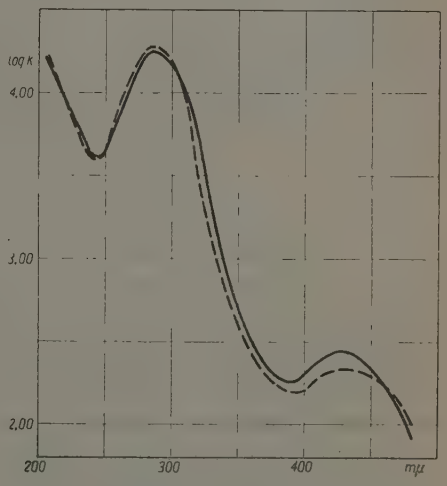
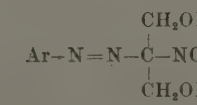


Fig. 2. 16*a* —, 16*b* – – –

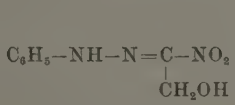
TABLE II

Compounds No.	λ min	ε	λ max.	ε	λ min.	ε	λ max.	ε
2a.	249–50	3230	291	15810	355	118.4	405–6	320
2b.	246–8	2850	291–5	12260	353–7	96.8	405	261.4
2c.	247–50	2770	294–7	15790	352–5	116.6	400–5	304
16a.	240–2	4420	286–8	19630	385	180.8	430–5	248.5
16b.	242–4	4510	285	18010	390–5	158.0	430–5	233.5

The azocompounds (III), when subjected to careful hydrolysis with alcoholic hydrochloric acid, formed the corresponding ketone or aldehyde as well as arylazonitrodiols (IV) – compounds so far unknown. They cannot be prepared by the action of diazocompounds on corresponding diols [11].



(IV)



(V)

The arylazonitrodiols (IV) are yellow-coloured products; their m.ps. and yields are tabulated below (Table III):

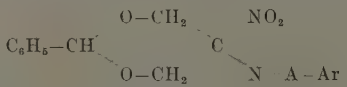
According to R. Kowalik and E. Czerwińska, products (IV) possess fungicide properties tested *in vitro* against *Fusarium culmorum*, *Alternaria solani* and *Rhizoctonia solani*, the fungicide concentration being 0.01% in compound (25) and 0.1% in compounds (24) and (27).

TABLE III

Compounds (IV) No.	Ar	Melting points (with decomp.) (°C.)	Yield per cent
24.	C_6H_5	97–99	82.0
25.	C_6H_4–Cl–*p*	97–98	72.0
26.	C_6H_4–NO_2–*p*	114–116	73.6
27.	C_6H_4–CH_3–*p*	95–97	65.6
28.	$C_{10}H_7$–β	107–108	68.9

Product (24), when warmed with aqueous potassium hydroxide and then acidified with sulphuric acid, formed phenylhydrazones of ω-nitroglycolaldehyde (V).

Compounds (IV) can be transformed into cyclic acetals (VI) (5-nitro-2-phenyl-1,3-dioxane) when warmed with benzaldehyde, the water of the reaction being removed, like the azeotrope, with benzene.



(VI)

The authors are much indebted to R. Kowalik and E. Czerwińska of the Institute of Intermediates and Dyestuffs, Warsaw, for carrying out experiments on the fungicide properties of some of the diols.

INSTITUTE OF ORGANIC SYNTHESIS, POLISH ACADEMY OF SCIENCES
DEPARTMENT OF ORGANIC TECHNOLOGY, INSTITUTE OF TECHNOLOGY, WARSAW

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CHEMISTRY

The Action of Salicylhydroxamic Acid and Some of Its Derivatives on Pathogenic Fungi *in vitro*

by

H. HALWEG and P. KRAKÓWKA

Communicated by T. URBAŃSKI at the meeting of May 16, 1955

In connection with the interest aroused by salicylhydroxamic acid and its derivatives in the treatment of tuberculosis [1] – [11] the authors of the present paper resolved to investigate the influence of these substances on pathogenic fungi.

Thus they analysed the effect of salicylhydroxamic acid (*T*2), sodium salt of salicylhydroxamic acid (sodium salt *T*2), 5-bromosalicylhydroxamic acid (*T*40) upon the following pathogenic fungi: *Trichophyton gypseum*, *Epidermophyton rubrum*, *Achorion Schoenleini* and *Candida albicans*.

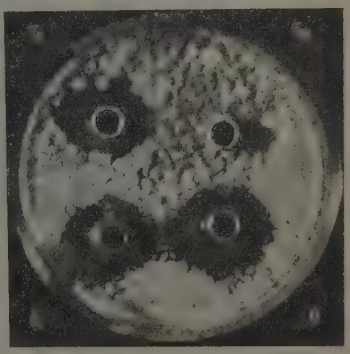

Fig. 1. Effect of *T*2, *T*40 and the antibiotic substance *Q* upon *Achorion Schoenleini*

In order to establish the fungistatic action of the above compounds, preliminary investigations were carried out by means of the cylinder-plate method. For determining the checking concentrations the dilution method was applied, a fluidal nutrient medium adapted for fungi cultivation being used. The cylinder-plate method was used to investigate the action of sodium salts of salicylhydroxamic and of 5-bromosalicylhydroxamic acid.

I. In the cylinder-plate method there was used 1.5% of Sabouraud agar $pH = 5$ with glucose. A suspension of the appropriate fungus in a physiological NaCl solution was inoculated on the agar surface on which the cylinders were placed. The suspension was prepared in a flask with beads. On the next day after inoculation of the fungus, an aqueous solu-

tion of sodium salt *T*2, of 2.5 mg./ml. concentration, was poured into one set of cylinders, and a saturated solution of *T*40 containing 0.033 mg./ml. of the substance with an equivalent quantity of NaOH, into another. The cultures were stored at a temperature of 37°. Growth of fungi followed in 3 days.

It the case of the *Achorion Schoenleini* culture, checking zones of 0.8—1.0 cm. radius were found around the cylinders containing sodium salt *T*2, and checking zones of 0.2—0.5 cm. radius in the case of *Epidermophylon rubrum* and *Trichophyton gypseum* cultures. No checking action was observed around the cylinders containing the saturated *T*40 solution with NaOH. Sodium salt *T*2 and *T*40 did not check the growth of *Candida albicans*.

In these experiments the effects of *T*2 and *T*40 were compared with those of the antibiotic substance *Q* obtained from the *Pseudomonas fluorescens* strain cultivated by the authors, and revealing an antibiotic action against some pathogenic fungi (Fig. 1).

II. In order to determine the concentrations checking the growth of pathogenic fungi, a dilution method was applied, fluid culture media being used. This method was adapted to the investigations into the action of fungistatic substances in the following manner: filter paper folded like a concertina was inserted into test-tubes measuring 16×116 mm; on top of the filter paper was placed a circle of hard filter paper (Fig. 2).

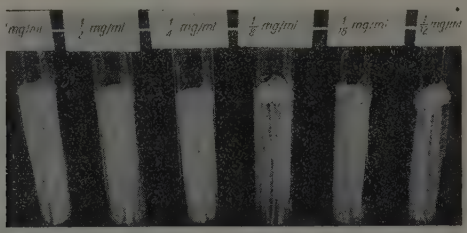

Fig. 2. Checking the growth of *Achorion Schoenleini* by sodium salt *T*2 (dilutions' method)

Into each of the test-tubes there was poured 6 ml. of Sabouraud culture medium containing different quantities of the investigated compound. Each test-tube was inoculated by means of 1 drop of homogeneous fungus suspension in physiological NaCl solution.

The highest concentration used of salicylhydroxamic acid (*T*2) and its sodium salt equalled 1 mg. per 1 ml. of the culture medium. As *T*40 is not readily soluble in water, it was necessary to add an equivalent of NaOH. Solutions with an initial concentration of 1 mg. per 1 ml. of the medium were applied. The *T*2 solutions in the Sabouraud medium had a *pH* of 6—6.5, which was tested colorimetrically, sodium salt *T*2 had

a *pH* of 7—7.5, and the *pH* of solution of *T*40 with NaOH amounted to 7—8.

In order to compare the various actions of *T*2, *T*40 and their sodium salts with those of salicylic acid and sodium salicylate, there were prepared the appropriate series of dilutions of these compounds with an initial concentration of 1 mg. per 1 ml. of the medium. Fungistatic action was tested in relation to the following pathogenic fungi: *Epidermophyton rubrum*, *Trichophyton gypseum*, and *Achorion Schoenleini*. The observation period was 10—12 days (Table I).

TABLE I

Compound name	Concentration causing total suppression of fungi growth in mg. per ml. of medium		
	Achorion Schoenleini	*Epidermophyton rubrum*	*Trichophyton gypseum*
Salicylhydroxamic acid (*T*2)	0.25—1.0	0.5	0.25—1.0
Sodium salt of *T*2	0.25—0.5	0.25—0.5	0.25—0.5
5-bromosalicylhydroxamic acid (*T*40)	—	—	—
Salicylic acid	—	—	—
Sodium salicylate	—	—	—

— indicates absence of fungistatic action

The present investigations show that salicylhydroxamic acid and its sodium salt, with a concentration of 0.25 — 1 mg. per 1 ml. of the culture medium, totally check the growth of the pathogenic fungi, *Achorion Schoenleini*, *Trychophyton gypseum* and *Edipermophyton rubrum*. 5-bromosalicylhydroxamic acid, in the concentrations used, resulted only in a certain inhibition of the fungi growth. Salicylic acid and sodium salicylate, in concentrations of 1 mg. per 1 ml. of the culture medium did not suppress the growth of the investigated fungi.

The drugs, *T*2 and *T*40, used by the authors in their investigation, were supplied by the Organic Synthesis Laboratory of the Institute of Tuberculosis.

The strains of skin fungi were recived from the Dermatology Clinic of the Medical Academy in Warsaw and from the Bacteriological Laboratory of No. 2 Hospital in Warsaw.

Further investigations on the fungistatic action of other salicylhydroxamic acid derivatives are in progress.

MYCOLOGICAL LABORATORY OF THE INSTITUTE OF TUBERCULOSIS, WARSAW

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CHEMISTRY

On Ultraviolet Absorption Spectra of Some β-Halogen Derivatives of β-Nitroalcohols

by

W. SOBÓTKA, T. URBAŃSKI and Z. ECKSTEIN

Communicated by T. URBAŃSKI at the meeting of May 16, 1955

One of the authors of the present paper recently put forward a hypothesis as regards the structure of alcohols obtained by adding formaldehyde to nitroparaffins [1]. This hypothesis was based on data obtained from an examination of ultraviolet absorption spectra and suggested the

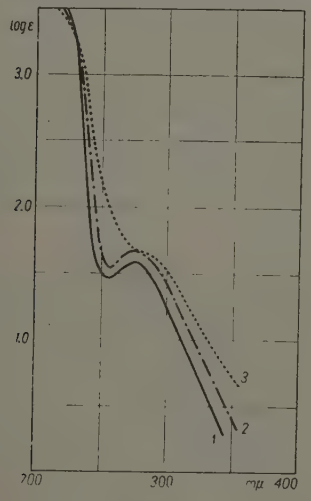

Fig. 1

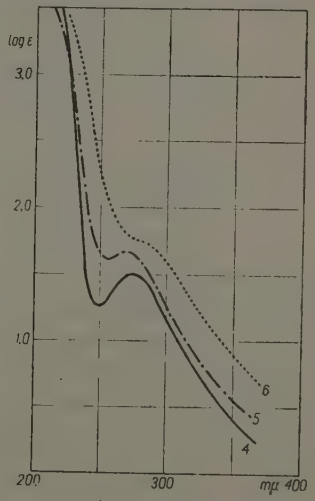

Fig. 2

existence of chelate rings between the nitrogroup and the alcoholic group (or groups) through the formation of hydrogen bonds.

The experiments here described were concerned with a group of chloro-or bromoderivatives of nitroalcohols, and our purpose was to find out the influence of chlorine or bromine on the ultraviolet absorption spectra.

A series of compounds (I) were prepared by adding aldehydes to nitromethane, forming next sodium salts of nitroalcohols which were subjected to the action of chlorine or bromine. In general the products thus obtained are known to the literature [2]-[10]. However, their boiling points, densities and refractive indexes were now determined in order to complete the existing data. Molecular refractions were also calculated from the refractive indexes and from the structural formulae. All the data are collected in Table I, together with those given by the literature. Compounds (5) and (6) have not as yet been described in the literature.

(I) $R-\underset{OH}{CH}-\underset{X}{CH}-NO_2$

TAB

No.	R	X	Boiling points	d_{20}
1	CH_3-	H–	72.5–73°/0.5 *)	1.1906
2	CH_3-	Cl–	71°/0.6	1.3645
3	CH_3-	Br–	90–90.5°/1.7	1.7485
4	CCl_3-	H–	45° **)	–
5	CCl_3-	Cl–	103.4°/0.7	1.7081
6	CCl_3-	Br–	104.6°/0.8	1.9834
7	C_2H_5-	H–	82.5°/1.2	1.1353
8	C_2H_5-	Cl–	89°/2	1.2793
9	C_2H_5-	Br–	94.5°/1	1.5941
10	$n-C_3H_7-$	H–	80.6°/0.6	1.0908
11	$n-C_3H_7-$	Cl–	87°/1	1.2286
12	$n-C_3H_7-$	Br–	34.5–35° **)	–
13	$(CH_3)_2CHCH_2-$	H–	90°/1.1	1.0587
14	$(CH_3)_2CHCH_2-$	Cl–	79°/0.5	1.1852
15	$(CH_3)_2CHCH_2-$	Br–	107–108°/1.2	1.4386

*) pressure in mm. Hg. **) m.p.

The most typical absorption curves were obtained with derivatives of 1-methyl-2-nitroethanol (compounds 1, 2 and 3) and 1-trichloromethyl-2-nitroethanol (compounds 4, 5, 6). They are shown on the diagrams (Figs. 1 and 2). It is interesting to note the difference between the absorption curves of compounds (1) and (4). Three atoms of chlorine introduced into the methyl-group produce a deepening of the maximum and a lowering of the coefficient of extinction.

Table II furnishes data concerning the maxima and minima of the absorption curves of all compounds in ethanol solutions.

LE I

n_D^{20}	Molecular refraction calculated		References
	from the structural formula	from experimental data	
1.4383	23.29	23.16	[2] b.p.=70–74°/0.2–0.8 mm. Hg $n_D^{20}=1.4412$
1.4603	28.06	27.93	[3] b.p.=91–92°/10 mm. [2] b.p.=89–91°/10 mm.
1.4930	30.93	30.57	[2] $n^{20}=1.493$
—	—	—	[4] m.p.=44–46°
1.5146	42.67	42.84	—
1.5361	45.56	45.17	-
1.4435	28.00	27.90	[8] b.p.=75°/2mm; [5]b.p.=93°/11mm $d^{25}=1.1303$ $n_D^{15}=1.4425$
1.4600	32.77	32.85	[6] b.t.=97°/9 mm; $R_{MDcal}=32.6$ $d_1^{20}=1.2827$ $R_{MDfound}=32.54$ $n_D^{20}=1.4548$
1.4860	35.67	35.65	[7] b.p.=111–112°/12 mm.
1.4439	32.71	32.39	[8] b.p.=85°/2 mm. $d^{25}=1.0810$ $n_D^{25}=1.4439$
1.4575	37.48	37.18	[9] m.p.=38°
—	—	—	[7] b.p.=119–120°/13 mm.
1.4474	37.23	37.14	[10]
1.4586	41.85	41.83	[10]
1.4837	44.79	44.93	[10]

It is clear that the introduction of bromine to the carbon attached to the nitrogroup considerably reduces the intensity of the maximum of absorption characteristic for the nitrogroup. Instead of the maximum, only a bend of the curve in the neighbourhood of 270-280 mμ. was noticed. This is probably produced by the steric effect of bromine upon the nitrogroup attached to the same carbon.

TABLE II

Characteristic of the absorption spectra

No.	λ min	ε	λ max	ε
1	251–3	28.2	275–6	38.3
2	255–6	34.8	277	46.5
3	—	—	280 *)	51.7
4	247	16.7	276	29.5
5	255	42.5	270	51.0
6	—	—	277 *)	64.5
7	253–6	40.2	272–5	45.1
8	258–260	41.3	275–8	50.8
9	—	—	280 *)	52.9
10	255–7	37.1	275	46.5
11	258	46.7	276–7	57
12	—	—	276–7 *)	57.5
13	255	42	275	51.6
14	260	55.3	277–80	70.3
15	—	—	277–8 *)	142.0

*) the bend

A similar steric effect of three bromine atoms upon the nitrogroup attached to the same carbon was noticed in the case of bromopicrine [11]. It is clear from our experiments that one bromine atom is sufficient to produce this effect.

It is well-known that the ionic radius of bromine is much larger than that of chlorine and very likely is sufficiently long to produce the steric effect mentioned above.

We are much indebted to J. Świętosławska, D. Ciecierska and K. Gorczyńska of the Institute of General Chemistry, Warsaw, for carrying out experiments on ultraviolet absorption spectra in a Beckmann spectrophotometer.

INSTITUTE OF ORGANIC SYNTHESIS, POLISH ACADEMY OF SCIENCES, WARSAW

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CHEMISTRY

Cathodic Lead Disintegration

by

H. ANGERSTEIN

Communicated by M. ŚMIALOWSKI at the meeting of May 16, 1955

It is a well known fact that during electrolysis of aqueous solutions of alkalo-metal salts, when there are large current densities, the lead cathode undergoes disintegration, and colloidal lead and lead powder are formed [1], [2].

It is reasonable to suppose that the mechanism of this phenomenon consists in one of the following processes:

1) disintegration caused by the mechanical action of hydrogen penetrating to the metal during electrolysis;
2) formation on the cathode of volatile lead hydrides, which, after abandonment of the electrode, undergo decomposition in the solution and form colliodal lead (Salzberg's hypothesis [2]);
3) the combining of lead with the metals deposited from the solution during electrolysis to form alloys or intermetallic compounds which are afterwards decomposed by water.

The aim of the present work was to determine which of the above processes is the actual cause of this phenomenon.

Experimental part

Method. The experimental part consisted in investigating the dependence, during electrolysis, of the lead cathode potential and the quantity of disintegrated lead on the current density, on the composition and concentration of the electrolyte and on certain additions to the electrolyte.

Electrolysis was carried out in an H-shaped vessel. The tube connecting both compartments, the cathodic, and anodic was filled with glass silk. Hydrogen was admitted through the cathodic compartment. A platinum plate served as the anode. The cathode was made from refined lead plate, free from arsenic. In order to ensure a uniform current density for the whole surface of the electrode, the latter was covered with an

acid-resisting varnish, all except for a circle ($\varnothing = 1$ cm.) which was left uncovered. Before measurement, the electrode was anodically polished in a solution of acet-anhydride and perchloric acid [3]. The amount of lead disintegrated during electrolysis was determined from the loss of the cathodic mass.

All the experiments were carried out at a temperature of 25.0°C.

Results of the experiments

I. In order to ascertain whether the first version of the reaction mechanism — i.e., disintegration of the metal through penetration of hydrogen to it — is the correct one, the author investigated to what extent the quantity of disintegrated lead, during electrolysis with a constant current density, depended on the introduction into the electrolyte (0.75 m Na_2SO_4 + 0.10 m H_2SO_4) of additional substances, i.e.,

a) substances decreasing the reaction rate of the combination of hydrogen atoms and thus facilitating the penetration of hydrogen to the metal (compounds of arsenic, antimony, tellurium and S^{-2}) [4],

b) dibenzyl sulphoxide, which checks the penetration of hydrogen to steel [5].

It was confirmend that the compounds added do not, within the limits of experimental error, have any influence on the amount of disintegrated lead, except for the arsenic compound, which checks disintegration.

Cathodic disintegration of lead, therefore, is not caused by hydrogen penetrating to the metal.

II. In order to throw further light on the phenomenon, we examined:

1. The dependence of the potential of the lead cathode on the composition of the solution during electrolysis when there is a constant current density. The following solutions were subjected to electrolysis: 1.0 m H_2SO_4, 0.10 m H_2SO_4 and 0.10 m H_2SO_4 with the addition of (a) 0.75 m Na_2SO_4, (b) 0.75 m K_2SO_4, (c) 0.75 m $MgSO_4$, (d) 0.75 m $Al_2(SO_4)_3$, (e) 0.75 m $(NH_4)_2SO_4$ and also a solution of lithium nitrate. It was noted that disintegration takes place when the following cations are present in the solution: Na^+, K^+, Li^+, Mg^{++}, Al^{+++}. The mode of disintegration, the cathode surface and the amount of disintegrated lead are all different in the presence of each of these ions, and so is the potential at which the reaction takes place (more negative in the presence of Mg^{++} ions, less so in the presence of Na^+ or K^+ ions). In solutions containing only MH_4^+ and H^+ cations, or only H^+, the cathode does not undergo disintegration.

2. Polarisation Curves. The polarisation curves were drawn of a lead cathode in the solutions: (a) 0.75 m Na_2SO_4 + 0.10 m H_2SO_4 and (b)

0.50 m Na_2SO_4+0.10 m H_2SO_4. The electrode potential was measured for each current density separately, and the electrode was polished before each measurement. The results of the experiments are presented in Fig. 1. The values obtained in the case of solution (a) are indicated by means of triangles, and in the case of solution (b), by means of dots. The course of the curves points to there being two processes of depolarisation. With small current densities hydrogen is evolved on the cathode (segment 1). After the limiting current density has been exceeded there follows the second process of depolarisation causing disintegration of the cathode (disintegration starts from points *A'*. and *A''*. on segment 3 of the polarisation curve). It can be seen from the diagram that in a solution with a greater number of Na^+ ions reaction takes place when the potential is more negative.

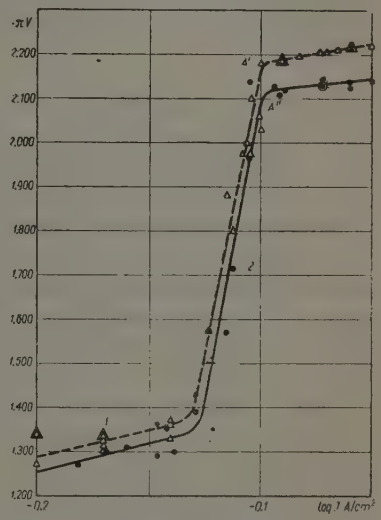

Fig. 1. ▬▪ 0.50 m Na_2SO_4+0.10 m H_2SO_4
▪▪▪▪△ 0.75 m Na_2SO_4+0.10 m H_2SO_4

3. Amount of disintegrated lead dependent on current density. The results of the measurements for the solutions 0.75 m Na_2SO_4 + 0.10 m H_2SO_4 and 0.50 m Na_2SO_4 +0.10 m H_2SO_4 are given in Fig. 2, which shows the ratio of the lead mass loss to the current density. It is evident that in the case of each of the solutions examined disintegration takes place, beginning from a certain current density I'_0 and I''_0. As the current density increases, the amount of disintegrated lead (Δm) grows linearly (from $\Delta m = 0$ for I_0) and is greater in the case of a solution with a smaller concentration of Na^+ ions. The scattering of points up to 30% is caused probably by the different rate at which the cathode potential becomes established.

Discussion of results

The polarisation curves obtained (Fig. 1) indicate the existence of two depolarisation processes. With small current densities there takes place only evolution of hydrogen arising out of the discharge of hydrogen ions (segment 1). Since there is a small concentration of hydrogen ions in the solution, the current is in large measure transferred by Na^+ ions. The density of the sodium ions at the cathode increases and the hydrogen ions have difficulty in reaching the latter. After the limiting current has

been attained, the cathode potential becomes more and more negative as the current density is increased (segment 2) until it attains a value at which a new process of depolarisation may take place, causing disintegration of the lead cathode (segment 3).

The second depolarisation process resulting in disintegration could be caused by different reactions. Salzberg proposes the following mechanism in explanation of this phenomenon:

a molecule of water is discharged on the cathode,

$$H_2O + e^- = H + OH^-.$$

The hydrogen thus formed reacts with lead, creating the hydride PbH_2 or PbH_4, which, after volatilisation from the cathode, undergoes decomposition in the solution. The following facts argue against this conception:

a. The fact that no disintegration takes place during electrolysis of solutions which do not contain metal cations. Salzberg mentions that disintegration takes place in acids but does not give any quantitative data nor any description of the experiments on which he based this statement. Certain data confirming this phenomenon are contained in a paper by Haber and Bredig, dating from 1898 [1]. In the experiments described in the present paper disintegration did not occur in sulphuric acid.

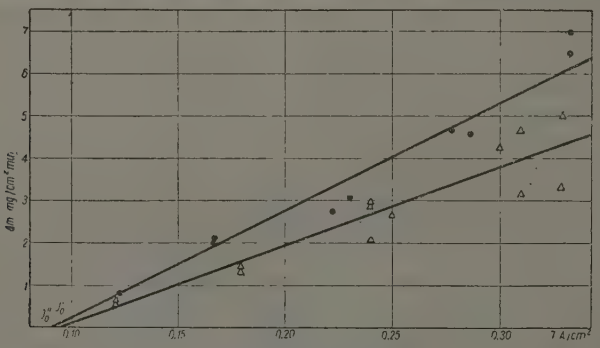

Fig. 2. ▪ 0.50 m Na_2SO_4+0.10 m H_2SO_4
△ 0.75 m Na_2SO_4+0.10 m H_2SO_4

b. The fact of the dependence already mentioned of the quantity disintegrated lead on the current density (the straight line in diagram 2 does not pass through the origin, as would appear from Salzberg's conception).

c. The fact that the number of electricity equivalents falling on 1 mol of disintegrated lead varies in accordance with the concentration of the metal cation in the solution and that therefore the composition of the compound which forms on the cathode also varies.

The above facts indicate that the second process of depolarisation has, most probably, the following mechanism: after the limiting current

density has been exceeded during electrolysis, and when the cathode potential has become sufficiently negative, there commences a discharge of the base metal ions appearing in the solution. The deposited metal combines with the lead on the surface of the cathode to form the alloy

$$(1) \qquad Me^{n+} + ne^- + xPb = MePb_x,$$

which then reacts with water, giving disintegrated lead, hydrogen, and the ions Me^{n+}, OH^-

$$(2) \qquad MePb_x + nH_2O = Me^{n+} + xPb + \frac{n}{2}H_2 + nOH^-.$$

Alloys formed from lead with sodium, potassium, lithium and magnesium are well-known; all react more or less powerfully with water, disintegrating even, with suitable concentrations, under the influence of damp from the air. The composition of the alloy formed on the surface of the metal as well as the cathode potential during disintegration depend on differences in the reaction rates both of the metal deposition and of the decomposition of the alloy. Reaction rate (1) is proportional to the activity of Me^{n+} in the solution and to the current density; reaction rate (2) — to the activity of the base metal in the alloy and to the activity of water. On the basis of the ascertained ratio of the amount of disintegrated lead to the concentration of sodium ions in the solution, it may be concluded that in the first moment of the reaction the discharge of ions is much quicker than the reaction of the decomposition of the alloy. The concentration of deposited metal is therefore increased on the surface of the electrode and at the same time the reaction rate of decomposition increases until it reaches a value equal to the rate of deposition of the metal. When a stationary state is reached in this way the alloy which decomposes is of a specified composition, and the cathode potential establishes itself. The greater the concentration of metal ions in the solution, the greater will be the deposition rate of the metal, and the stationary state will be reached with an alloy richer in base metal; the cathode potential during disintegration will therefore be more negative. Such a state was actually noted during the disintegration of a lead cathode in solutions containing sodium sulphate.

On the basis of the dependence of the amount of disintegrated lead on the current density, when there is a uniform current density over the whole surface of the cathode, it is possible to calculate the approximate composition of the alloy which have formed on the cathode. In the case of the solutions examined which contained Na^+ ions, the number of electricity equivalents falling on one mol of disintegrated lead was: for the solution 0.75 m Na_2SO_4 + 0.10 m H_2SO_4 — on an average 0.72, for the solution 0.50 m Na_2SO_4 + 0.10 m H_2SO_4 — on an average 0.52. An alloy which

decomposes on the electrode would have, therefore, in the first case, a quantitative composition of about 58% atom. Pb and 42% atom. Na, and, in the second case, about 66% atom. Pb and 34% atom. Na.

The author is indebted to Professor M. Śmiałowski for suggesting this problem and for his kind help and interest in this work.

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CHEMISTRY

Antiraoultic Properties of Some Concentrated Ternary Aqueous Solutions

by
M. SARNOWSKI, B. BARANOWSKI, J. ZYGADŁO

Presented by M. ŚMIAŁOWSKI on June 8, 1955

The relative depression of the vapour pressure of the solvent over an ideal liquid solution of a solid in water is given by Raoult's law:

$$\frac{n_0+n_1}{n_0+n_1'}=\frac{P_1'}{P_1}, \tag{1}$$

where n_0 is the number of moles of the solvent (water), n_1 and n_1' are the number of moles of a solid dissolved in two solutions, while P_1 and P_1' are the vapour pressures over these two solutions. If $n_1'=n_1+n_2$, where n_1 and n_2 are the uumber of moles of two various solids, then for some systems the following inequality may be fulfilled:

$$\frac{P_1'}{P_1}>1, \qquad \text{where} \quad \frac{n_0+n_1+n_2}{n_0+n_1}>1. \tag{2}$$

It follows that the water vapour pressure over a solution of a greater total concentration (a ternary solution) is higher than over a less concentrated solution (a binary solution). Ternary solutions fulfilling the inequality (2) will be here referred to as antiraoultic solutions.

It has been the aim of this work to describe the antiraoultic properties of several ternary water solutions and to show that the behaviour of such solutions cannot be explained satisfactorily by recent electrostatic theories.

Experimental method

The isopiestic method (isothermal distillation) was used. This consisted in gravimetric measurements of the differences in the weights of water of two isothermal solutions in ρpen vessels placed side by side in an enclosed space [1], [2],]3]. One vessel always contained a binary solution of an electrolyte, while in the other vessel to the same binary solution a solid

anhydrous non-electrolyte or electrolyte was added. For measurements, several grams of each solution were used. After the vessels were left standing side by side at a constant temperature in an enclosed space for some time the weight of water in both vessels changed. When the time period was several days, the changes in weight often reached several hundred milligrams. It has been shown on solutions of known vapour pressure that this corresponds to differences in pressures over a binary and a ternary solution of the order of not more than a few millimetres of mercury. No attempts were made to wait till a state of isopiestic equilibrium was reached. It is obvious that the weight of the solution with lower water vapour pressure increased, while the solution with greater vapour pressure lost the solvent as a result of isothermal distillation. It may be assumed as a first approximation that the changes in the weight of the solvent in the two vessels, when observed in identical experimental conditions and after the same time, were proportional to the difference in the vapour pressure over the two solutions. This seems likely as the difference in vapour pressures of the two solutions is known to be small.

Results

It has been shown in the course of many experiments, [1], [2], [3], that numerous binary aqueous solutions of electrolytes (e. g. $CaCl_2$, $Ca(NO_3)_2$, $MgCl_2$, $Mg(NO_3)_2$, $LiNO_3$) exist which, when solid urea is added to them, display the following properties:

a. When solid urea is added to a dilute solution of an electrolyte, then the water vapour pressure over the ternary solution is always lower than over binary solution, and this difference of vapour pressure increases as more urea is added (the raoultic region).

b. The addition of urea at a certain concentration level of the electrolyte in solution causes an increase in water vapour pressure. At first, as more urea is added, the vapour pressure increases: when the maximum pressure is reached it falls again (the antiraoultic region).

c. It hat been found that a certain concentration or a concentration region exists at which when urea is added the water vapour pressure is changed only slightly (the transition region).

On the basis of results so far obtained it can be said that the transition concentration — or the concentration region of the binary solution — at which the addition of urea changes only slightly the vapour pressure, depends both on the anion and the cation of the electrolyte.

The three curves here presented illustrate the changes of the weight (Δm in grams) in the vessel containing the ternary solution in the case of one or more initial electrolyte solutions. These changes are presented as a function of the molar ratio of urea to the electrolyte (n_u/n_{el}) in the ternary solution. In the positive section of the axis of ordinates the loss in the weight

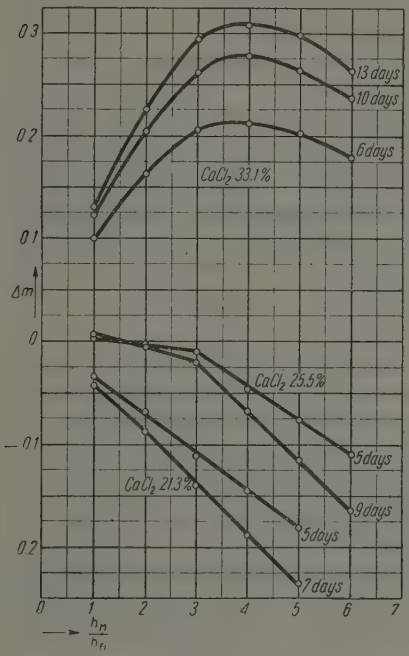

Fig. 1

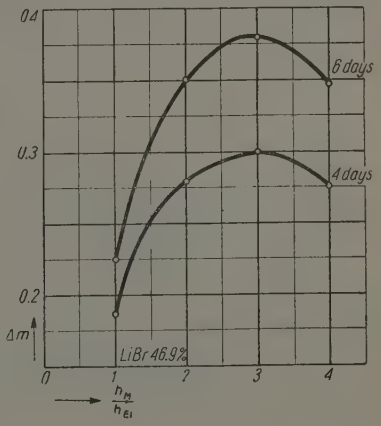

Fig. 2

of the solvent from the ternary solution is given (the antiraoultic region). In the negative section the increase in the weight of the solvent from the ternary solution is included (the raoultic region). The time after which the change in the weight of water was measured is given on each graph.

The curve in Fig. 1 is plotted for the $CaCl_2$—$CO(NH_2)_2$—H_2O system and shows the changes in the weight of water in a vessel containing the ternary solution for three initial calcium chloride concentrations. These three concentrations are 21.5, 22.5, and 33.1 per

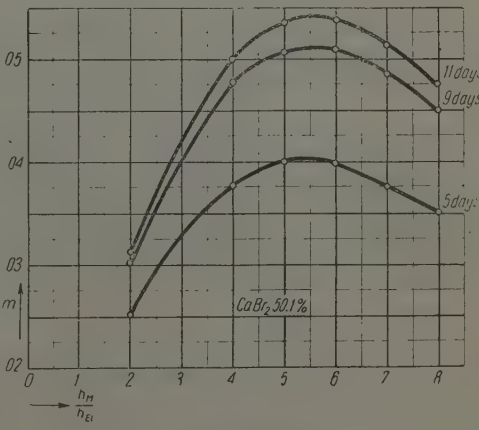

Fig. 3

cent and correspond to the raoultic, transition and the antiraoultic regions, respectively.

The results for the systems $CaBr_2 - CO(NH_2)_2 - H_2O$ and $LiBr - CO(NH_2)_2 - H_2O$ refer only to the antiraoultic region.

A more detailed and fuller report of the experiments is given in another publication [3].

Antiraoultic properties when urea is added have been also observed in binary water solutions of the following electrolytes: LiI, $MgBr_2$, $Cd(NO_3)_2$, $Mn(NO_3)_2$, $ZnCl_2$ and $Zn(NO_3)_2$ [2]. The antiraoultic effect may also be obtained when a solid electrolyte is added to a binary water solution of another electrolyte [1], [2] or when to a solution of an electrolyte a non-electrolyte other than urea, is added.

Discussion

From the point of view of thermodynamics the antiraoultic properties are closely associated with the so-called salting-in, i.e. the decrease in the activity coefficient of a non-electrolyte in a solution of electrolytes. Recent electrostatic interpretations of these effects [4] are based primarily on Debye's theory [5] which relates the salting-in or the salting-out effect to the change in the dielectric constant of the solvent when the non-electrolyte is added.

As urea increases the dielectric constant of water, the increase in the water vapour pressure after this non-electrolyte is added to an adequately concentrated solution of an electrolyte may be explained on the basis of Debye's theory [5].

Provisional calculations show that for electrolytes of the type of $Ca(NO_3)_2$ already at a concentration of 2-3 mole per litre the antiraoultic effect can be expected by adding urea. However, on the basis of Debye's theory and its later amendments, it is impossible to explain the extremes which apper in the curve representing the changes in water vapour pressure in relation to the molar ratio of urea to the electrolyte (Figs. 1, 2, and 3). Moreover, Debye's theory does not explain the antiraoultic effect when saccharose is added to a concentrated solution of an electrolyte. According to electrostatic interpretation, salting-out should then take place, similarly as it does in dilute solutions [5]. Furthermore, it would be difficult to explain on the basis of Debye's theory the antiraoultic properties in ternary solutions of electrolytes.

INSTITUTE OF SYNTHETICAL CHEMISTRY, LABORATORY IN TARNÓW

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CHEMISTRY

The Relation between Antiraoultic Properties of Some Ternary Aqueous Solutions and Complex Formability

by

M. SARNOWSKI, B. BARANOWSKI, J. ZYGADŁO

Presented by M. ŚMIAŁOWSKI on June 8, 1955

In earlier papers reports have been made on the antiraoultic properties of some solutions [1]–[3]. Moreover, it has been pointed out that it is difficult to explain these properties on the basis of recent electrostatic theories of salting-out effects [4].

The aim of the present paper is to show the relation which exists between the antiraoultic properties and the ability to form complex compounds in some ternary systems. On the basis of this relation an attempt will be made at explaining qualitatively the effects observed.

Complex formability in antiraoultic systems

By limiting the problem to the cases so far investigated it can be stated that ternary aqueous solutions containing an electrolyte and a non-electrolyte and displaying antiraoultic properties are characterized by the ability to form solid complex compounds. Similarly in the case of ternary solutions of electrolytes the antiraoultic properties are associated with the formation of solid double salts.

In the course of a research on the changes in water vapour pressure of antiraoultic systems it has been found that, in fixed experimental conditions, the change in the weight of the solvent in one solution has an extreme corresponding to a definite urea to electrolyte molar ratio [3]. In several cases it has been shown that the extreme appears in the vicinity of the molar ratio corresponding to the solid complex compound in which the urea content is greatest. This is shown more clearly by the table on the following page.

The close relation between the antiraoultic properties and the ability to form complex compounds is confirmed by the fact that on the basis of this vapour pressure "criterion" a number of complex and double

compounds have already been obtained which have not been reported previously. Some of these have been described in recent publications, [5]–[7], and a report on the others is now being prepared for publication. Some compounds, as for instance compound $Ca(NO_3)_2.CO(NH_2)_2.3H_2O$, have properties which may be of commercial interest – e.g., low hygroscopicity [5]. Several of the newly obtained compounds are being now examined roentgenographically.

Electrolyte in solution (concentration in weight per cent)	Urea to salt ratio in the vicinity of the extreme	Composition of complex compound when urea content is geatest
$CaCl_2$ 33.1	4:1	$CaCl_2.4CO(NH_2)_2$
$CaBr_2$ 50.0	5–6:1	$CaBr_2.6CO(NH_2)_2$
$Mg(NO_3)_2$ 37.6	3–4:1	$Mg(NO_3)_24CO(NH_2)_2$
LiBr 46.9	3:1	$LiBr.3CO(NH_2)_2$

Attempted interpretation of antiraoultic properties of ternary solutions of an electrolyte and a non-electrolyte.

In all interpretations of the salting-in and salting-out effects based on recent electrostatic theories, the solvent is considered as a continuous medium. However, in opposition to this approach an interpretation of the antiraoultic properties may be made in which the direct interaction between the solvent and the added non-electrolyte molecules with ions is taken into account. It is significant that those electrolytes which in solution with non-electrolytes display antiraoultic properties are known for their affinity to hydration. In recent theories of ion solvation in water solutions [8], [9] it is assumed that there is a first hydration shell strongly attached to the ions. The following interpretation of the anitraoultic properties may be made.

When to a solution of an electrolyte urea is added, its molecules may either remain free or they may displace water molecules from the hydration shell. The first effect will dominate in dilute solutions and will cause a decrease in water vapour pressure, while in concentrated solutions the latter will prevail and may be regarded as responsible for producing the antiraoultic properties. This would explain also the transitional concentration between the raoultic and the antiraoultic regions.

As the amount of urea in the antiraoultic region increases, the solvation shell, which is being formed, may reach a state of saturation. As a result, the number of urea molecules unattached to ions will increase if the urea component in the solution increases further, and may thus be the reason why extremes appear. Consequently, the antiraoultic properties cannot be explained solely by the interaction between the electrolyte and the non-electrolyte which form complex molecules in the solu-

tion but the active co-operation of water molecules in this process must also be accepted.

This interpretation seems most plausible if it is remembered that antiraoultic properties are observed in solutions of relatively high concentrations, when most water molecules already enter into the composition of ionic hydrates. The correlation between the composition corresponding to the previously mentioned extreme and the composition of the solid complex compound seems to indicate a close relation of molecules appearing in the liquid and solid phases. This is so, because according to Job's principle [10] of continuous changes, the extreme may appear in the vicinity of the stoichiometric composition of molecules present in the liquid phase. The results which have been reported in another paper [3] are an example of how the isopiestic method may be applied for research on complex molecules in ternary solutions. The present interpretation, based on the assumptions that in the hydration shell the molecules of water and of non-electrolyte are exchanged, is further supported by the fact that the boundary concentration corresponding to the transition from the raoultic to the antiraoultic regions depends both on the third component and the degree to which the ions of the electrolyte are hydrated.

In this manner, the greater the ability for hydration of the electrolyte, the greater is, on the whole, the molar fraction of water in the transition concentration. Antiraoultic properties in ternary solution of an electrolyte and non-electrolyte are, therefore, to be expected in solutions in which the following conditions prevail: a) ion hydration is as great as possible; b) the attraction between ions and the molecules of the non-electrolyte is strong; c) the solubility of the electrolyte is high, thus allowing the transition from the raoultic region. It must be noted that a similar interpretation was suggested by Centnerszwer [11] to explain the antiraoultic properties observed in ebullioscopic measurements. Moreover, as it can be seen in the case of magnesium sulphate, the dissociation of the electrolyte in concentrated solutions should be as great as possible [12].

Attempted interpretation of antiraoultic properties in ternary aqueous solutions of electrolytes.

Recent theories of solutions of strong electrolytes [13] take into account not only the influence which the volume of ions has on the partition function, but also the possiblity of incomplete dissociation in solutions. If, besides, the latter effect it is assumed that the molecules of double salts may be present in a solution, then antiraoultic properties in ternary solutions of electrolytes may be explained by a decrease in the number of water molecules in the composition of hydrates. Moreover, this interpretation would have to be based on the assumption that the molecules of double salts are less hydrated than the component ions or the undissociated molecules of the electrolyte. Some support for this last assumption

may be found in that the number of water molecules tied up in solid double salts is on the whole smaller than in solid component salts.

The interpretation suggested here assumes a close relation between antiraoultic properties and the preferential solvation in three-component systems [14]–[16].

The existence of complex molecules in similar ternary solutions has been demonstrated many times with various physico-chemical methods [17]–[19].

Fuller details of the interpretation outlined here will be published elsewhere [12].

The authors wish to express their most sincere gratitude to Professors Bobrownicki and Gumiński and to Docent Stobiecki for the collaboration between the Department of Theoretical Chemistry of the Jagiellonian University and the Institute of Synthetical Chemistry which they initiated and organised.

INSTITUTE OF SYNTHETICAL CHEMISTRY, LABORATORY IN TARNÓW

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Lower Carboniferous Fauna in the Culm Facies of the Eastern Upper Silesian Coal Basin

by

S. CZARNIECKI

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In the vicinity of the village of Zalas, ten kilometres to the south of Krzeszowice there are several outcrops of the Carboniferous beds composed of clay and sandy shales. Earlier writers, as for instance E. Tietze [1], S. Zaręczny [2], and others, classified them in the lower members of the Upper Carboniferous. In 1907, three prospective boreholes were sunk in the area, and the results were described by R. Michael [3]. In one of the boreholes in the western part of the village of Zalas the drill, after piercing, at a depth of 176 metres, a thin bed of limestone with Lower Carboniferous Spirifers, entered a series of shales considered by R. Michael as typical Culm. Two kilometres south of Zalas in the Orlej Gorge near the village Głuchówki there is a small outcrop of black shales classified by R. Michael as the Lower Carboniferous. This is the most south-easterly outcrop of the Carboniferous beds in the fringe of the Upper-Silesian Basin. R. Michael's opinion was questioned by Petrascheck [4], who considered them as analogous to the Ostrawa beds of Upper-Carboniferous. As paleontological evidence was not available, both opinions were based on lithological analogies.

In 1953, a deep trench was cut in a SW-NE direction in the quarry at Orlej and this exposed a 120 metre-deep profile of the Carboniferous shales with limestone intercalations. In these beds fossils in great profusion have been found by S. Dżułyński [5].

The strike of the Carboniferous strata in the exposure is 350° and their dip is 70—80° in a north-westerly direction. To the west the Carboniferous series is truncated by a fault the direction of which is 160°. Along the fault, the series contacts with Lower Jurassic clays, while to the east it contacts with an intrusion of porphyry which has altered the colour and strongly silicified the adjacent shales. The limestone intercalations are situated in the western, stratigraphically higher, part of the bed. One of them is located 85 metres to the west of the porphyries and its thickness

is 0.45 metres; the other is 12 metres above the former and its thickness is 0.20 metres. Fossils occur in the strata surrounding the limestone. The distribution of the organic remains in these measures will now be described.

The fauna in the shales underlying the limestones is fairly rich in specimens but poor in species. It consists of pelecypods, snails, and *Chonetidae*. In the limestone beds there are numerous crinoidal fragments and scarce, though well preserved, braciopods, trilobites and corals. Moreover in the lower and thicker limestone bed there are numerous colonies of stromatopores. The greatest development of fauna occurs in the shales resting on top of the two limestone intercalations, though, in each case, the fossil association is markedly different.

The fossiliferous stratum resting on top of the lower of the two limestone beds is only 10 centimetres thick and contains in profusion fragments of brachiopods, *Bryozoa*, pelocypods, snails, corals and trilobites. The most common are here the colonies of *Bryozoa* from the genus *Fenestella* and large *Spiriferae*. I have also found several well preserved specimens of *Blastoidea*.

The fossiliferous shales overlying the upper limestone intercalation are 80 centimetres thick. Their fauna is very well preserved. They consist of crinoidal fragments, brachiopods (*Productidae* and *Chonetidae*) and corals, as well as the less frequent snails, palecypods, trilobites, *Orthoceratidae*, and *Hyolithes*. Gradually the fauna becomes scarce and in the upper part of the stratum consists only of snails, pelecypods, *Chonetidae* and *Nautiloidea* forms. In the remaining shale strata there are either no fossils whatsoever, or single badly preserved specimens are found only occasionally. The very few plant fragments are small and unrecognisable.

Near the bottom of the uncovered profile there are in the shales two lenses of conglomerates composed of sharp-edged more strongly consolidated shale fragments, partly rounded porphyry fragments, and large porphyry blocks containing numerous shale fragments.

So far only the *Choneteidae* and *Productidae* from the upper fossiliferous strata have been studied. These include the following species:

Plicochonetes tricornis v. Semenev
Plicochonetes waldenburgianus Paeck
Paeckelmania polita M'Coy
Paeckelmania coninckiana v. Semenev
Productus (*Krotovia*) *spinolosus* Sow. *var. granulosa* Phillips
Productus (*Thomasella*) *margaritaceus* Phill.
Productus (*Pugilus*) *pugiloides* Sarytchewa
Productus (*Antiquatonia*) *costatus* Sow.
Productus (*Eomarginifera*) *tissingtonensis* Sibly
Productus (*Eomarginifera*) *precursor* Muir-Wood
Productus (*Eomarginifera*) *setosus* Phillips.

From the species listed the genus *Plicochonetes* is very common in the Lower Carboniferous in England, Russia and Germany. According to Sokolska [6] the genus dies out completely by the end of the Lower Carboniferous. The species *Plicochonetes tricornis* v. Semenev and *Plicochonetes waldenburgianus* Paeck., occur in the Vizé deposits of the Moscow Basin and Lower Silesia.

Productus (*Thomasella*) *margaritaceus* Phill. is also very common, and does not appear later than in the Early Carboniferous. *Productus* (*Eomarginifera*) *tissingtonensis* Silby is an index fossil for the Vizé stage (zones D_2–D_3) in England. *Productus* (*Pugilus*) *pugiloides* Sarytchewa occurs only in the Uppermost Vizé strata of Lower Silesia and in the Uppermost Lower Carboniferous level (C_1 prt) of the Moscow Basin.

The remaining species listed are found both in the Lower Carboniferous and in the lower zones of the Upper Carboniferous, while the greatest development of such species as *Productus* (*Antiquatonia*) *costatus* Sow., *Chonetes* (*Peackelmania*) *coninckianus* v. Sem., and *Productus* (*Eomarginifera*) *precursor* Muir-Wood occurred at the time of the Vizé sedimentation.

It follows from the data assembled here that the shales from Orlej correspond to the topmost Vizé stage (zones D_2–D_3, according to the British classification) which are lacking – according to J. Jarosz [7] – in the limestone facies of the Dębnik Ridge. At the same time the results now reported support the opinion of J. Nowak and J. Zerndt [8]. These writers believe, that the Early Carboniferous deposits, lying to the west of the Carboniferous limestones stretching along the line Samborek-Dębnik-Siewierz, were developed as a Culm facies because the bottom of the sedimentation basin subsided in the direction of the River Odra synclinorium. The conglomerates near the bottom of the exposed profile containing rounded porphyry boulders with shale fragments indicate that intense volcanic activity occurred in the area as early as the Lower Carboniferous.

The Culm facies in the exposure at Orlej is the first to be supported by paleontological evidence on the east fringe of the Upper Silesian Basin. Moreover, the richness and the diversity of the fossils found there are seldom met with in such facies. In the material collected so far I have several thousands specimens of about a hundred species of macro-fauna, while washed samples also show very rich and diverse micro-fauna. For all these reasons the exposure in Orlej is of great significance for the study of the Lower Carboniferous sedimentation conditions and paleogeography on the east fringe of the Upper-Silesian Basin.

LABORATORY OF GEOLOGY AND STRATIGRAPHY, POLISH ACADEMY OF SCIENCES

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